Electronic Supplementary Information

Platinum-Catalyzed Reactions of Propargyl Carboxylates with Carbonyl-ene-nitrile Compounds Leading to *α*-Alkylidene-*N*-furylimines

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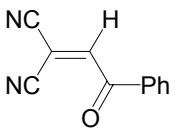
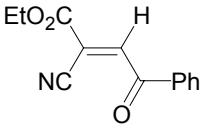
General Method. Unless otherwise noted, chemicals obtained from commercial suppliers were used without further purification. Solvents were dried by the usual methods and distilled before use. Propargyl carboxylates **1** and carbonyl-ene-nitrile compounds **2a** and **2b** were prepared according to the reported procedure.[1,2] All reactions were carried out under nitrogen atmosphere. NMR spectra were measured for solutions in $CDCl_3$ with tetramethylsilane as an internal standard (^1H and ^{13}C): the following abbreviations are used; br: broad, s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet. IR spectra were recorded with an FT-IR spectrometer. Melting points (mp) are uncorrected. Element analyses were performed at Microanalytical Center of Kyoto University. High-resolution mass spectra (HRMS) was measured with JEOL JMX-SX 102A spectrometer.

Preparation of Carbonyl-ene-nitrile Compounds 2c and 2d. A solution of phenylglyoxal monohydrate[3] (1.38 g, 10 mmol) and MS4A (2.0 g) in MeCN (20 mL) was added malononitrile (for **2c**) or ethyl cyanoacetate (for **2d**) (10 mmol), and the mixture was stirred overnight at 80 ^oC. The resulting mixture was filtered through short silica gel pad, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (hexane/AcOEt = 7/1–4/1) to afford corresponding carbonyl-ene-nitrile compounds **2c** or **2d** as yellow solids, respectively. **2d** was obtained as a single stereoisomer.



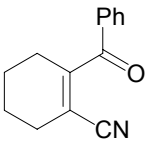
3,3-Dicyano-1-phenyl-2-propen-1-one (2c): A pale yellow solid; mp 115.1-115.6 ^oC. IR (KBr): 687, 778, 896, 1011, 1182, 1254, 1364, 1446, 1598, 1662 (C=O), 2211, 3428 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.59 (t, J = 7.7 Hz, 2H), 7.74 (t, J = 7.7 Hz, 1H), 7.98 (d, J = 7.7 Hz, 2H), 8.20 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 96.7, 110.3, 111.9, 129.1, 129.5, 134.3, 135.7, 151.2, 184.0. HRMS (FAB) calcd for $M+H^+$ of $C_{11}H_6N_2O$ 183.0558, found 183.0555.



Ethyl (*Z*)-1-benzoyl-2-cyanoacrylate (2d): A yellow solid; mp 63.6-64.2 ^oC. IR (KBr): 693, 756, 1002, 1094, 1265, 1448, 1595, 1671 (C=O), 1740 (C=O), 2214, 3460 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.42 (t, J = 7.3 Hz, 3H), 4.44 (q, J = 6.8 Hz,

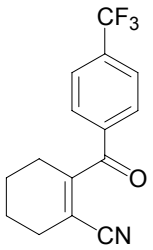
2H), 7.56 (t, J = 7.3 Hz, 2H), 7.69 (tt, J = 1.5, 7.3 Hz, 1H), 8.00 (dd, J = 1.5, 7.3 Hz, 2H), 8.44 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 63.7, 112.8, 115.5, 129.0, 129.2, 135.0, 135.1, 147.5, 160.4, 186.9. HRMS (FAB) calcd for M+H$^+$ of $C_{13}H_{11}NO_3$ 230.0817, found 230.0822.

Preparation of Carbonyl-ene-nitrile Compounds 2e and 2f.



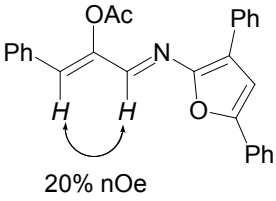
1-Benzoyl-2-cyanocyclohexene (2e): To a solution of 2-bromo-1-cyclohexenecarb-aldehyde (1.69 g, 9.0 mmol) in THF (10 mL) was added a solution of phenylmagnesium bromide (10 mmol) in THF (10 mL) at -78 ^{o}C under N_2. The mixture was stirred at -78 ^{o}C for 1 h, and then poured into saturated aqueous NH_4Cl solution (20 mL). The resulting mixture was extracted with AcOEt (20 mL×3), and the organic layer was dried over $MgSO_4$. The organic solvent was removed under reduced pressure to afford α-(2-bromocyclohexen-1-yl)benzyl alcohol (2.29 g, 9.0 mmol, quant.) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.55-1.76 (m, 4H), 2.07-2.09 (m, 1H), 2.23-2.32 (m, 1H), 2.55-2.60 (m, 2H), 6.04 (d, J = 3.4 Hz, 1H), 7.26 (t, J = 7.4 Hz, 1H), 7.34 (t, J = 7.4 Hz, 2H), 7.43 (d, J = 7.4 Hz, 2H). To a solution of α-(2-bromocyclohexen-1-yl)benzyl alcohol (2.29 g, 9.0 mmol) in CH_2Cl_2 (20 mL) was added Dess-Martin periodinane (3.82 g, 9.0 mmol) at 0 ^{o}C, and the resulting mixture was stirred at room temperature for 10 min. The organic solvent was removed under reduced pressure and the resulting white solid was filtered through short silica gel pad with Et_2O as an eluent. The residue was subjected to flash column chromatography on silica gel with hexane/AcOEt (v/v = 20/1) as eluents to afford 1-benzoyl-2-bromocyclohexene (2.30 g, 8.7 mmol, 97%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.77-1.89 (m, 4H), 2.34-2.36 (m, 2H), 2.61-2.64 (m, 2H), 7.49 (t, J = 7.3 Hz, 2H), 7.60 (t, J = 7.3 Hz, 1H), 7.95 (d, J = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 24.2, 29.6, 35.6, 120.2, 128.8, 129.6, 133.6, 134.5, 137.8, 197.6. To a solution of 1-benzoyl-2-bromocyclohexene (2.30 g, 8.7 mmol) in DMF (20 mL) was added CuCN (860 mg, 9.6 mmol), and the resulting mixture was stirred at 110 ^{o}C for 3 h. The reaction mixture was poured into water, and then the aqueous layer was extracted with AcOEt (50 mL×3). The combined

organic layer was washed with brine and dried over $MgSO_4$. The organic solvent was removed under reduced pressure and the residue was subjected to flash column chromatography on silica gel with hexane/AcOEt (v/v = 4/1) as eluents to afford 1-benzoyl-2-cyanocyclohexene **2e** (1.66 g, 7.8 mmol, 90% yield) as a colorless solid. mp 41.0-42.0 ^{o}C. IR (KBr): 690, 758, 1205, 1446, 1499, 1740 (C=O), 2912, 3420 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.75-1.79 (m, 4H), 2.39-2.42 (m, 2H), 2.42-2.47 (m, 2H), 7.49 (t, J = 7.8 Hz, 2H), 7.62 (t, J = 7.8 Hz, 1H), 7.87 (d, J = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.5, 20.8, 27.2, 27.6, 111.2, 117.0, 128.8, 129.4, 134.1, 134.5, 154.4, 196.0. HRMS (FAB) calcd for M+H^{+} of $C_{14}H_{13}NO$ 212.1075, found 212.1088.

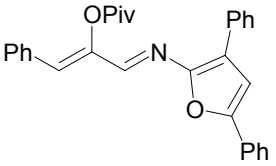


2-Cyano-1-cyclohexenyl (4-trifluoromethyl)phenyl ketone (2f): A pale yellow solid; mp 63.2-64.1 ^{o}C. IR (KBr): 687, 752, 1203, 1364, 1612, 1728 (C=O), 2910, 3428 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.80-1.82 (m, 4H), 2.45-2.48 (m, 4H), 7.77 (d, J = 7.8 Hz, 2H), 7.98 (d, J = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.6, 20.9, 27.5, 27.6, 112.7, 116.8, 123.3 (q, J = 273 Hz), 126.0 (q, J = 3.3 Hz), 129.8, 135.3 (q, J = 32.2 Hz), 137.5, 153.5, 195.0. HRMS (FAB) calcd for M+H^{+} of $C_{15}H_{12}F_3NO$ 280.0949, found 280.0947.

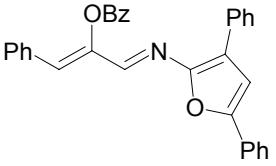
General Procedure for Platinum-catalyzed Reactions of Propargyl Carboxylates with Carbonyl-ene-nitrile Compounds. A solution of propargyl carboxylate **1** (1.2 mmol) and $PtCl_2$ (8.0 mg, 0.030 mmol) in toluene (1.2 mL) was added to carbonyl-ene-nitrile compound **2** (0.30 mmol), and the resulting mixture was stirred at 70 ^{o}C for 17 h. The resulting mixture was directly subjected to flash column chromatography on silica gel with hexane/AcOEt/ CH_2Cl_2 (v/v = 15/1/1) as eluents to afford the corresponding *N*-furylimine. The structures of products were determined by nOe experiments.



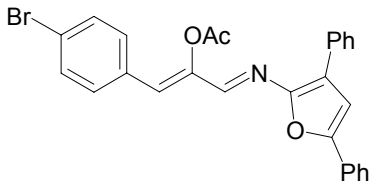
***N*-(2-Acetoxy-3-phenyl-2-propen-1-ylidene)-3,5-diphenyl-2-furanamine (3a)**: A yellow solid; mp 168.1-169.3 °C. IR (KBr): 689, 756, 929, 1129, 1206, 1449, 1493, 1753 (C=O), 3422 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 3H), 6.72 (s, 1H), 6.99 (s, 1H), 7.27-7.43 (m, 9H), 7.61 (d, J = 7.2 Hz, 2H), 7.72 (d, J = 7.2 Hz, 2H), 7.83 (d, J = 7.2 Hz, 2H), 8.32 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0, 107.4, 122.9, 123.9, 126.7, 127.2, 127.9, 128.0, 128.2, 128.7, 128.9, 129.1, 129.5, 129.9, 132.3, 133.4, 146.1, 146.4, 149.0, 150.3, 168.1. Anal. calcd for $C_{27}H_{21}NO_3$: C, 79.59; H, 5.19. Found: C, 79.41; H, 5.21.



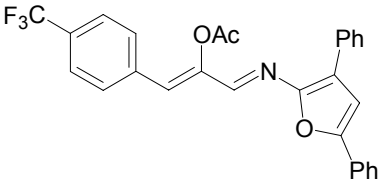
***N*-(2-Pivaloyloxy-3-phenyl-2-propen-1-ylidene)-3,5-diphenyl-2-furanamine (3b)**: A yellow solid; mp 175.2-176.0 °C. IR (KBr): 694, 761, 1114, 1270, 1480, 1744 (C=O), 3460 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.30 (s, 9H), 6.69 (s, 1H), 6.90 (s, 1H), 7.21-7.33 (m, 9H), 7.52 (d, J = 6.8 Hz, 2H), 7.64 (d, J = 7.3 Hz, 2H), 7.72 (d, J = 7.3 Hz, 2H), 8.31 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.4, 39.0, 107.7, 122.6, 124.0, 127.1, 128.0, 128.2, 128.2, 128.5, 128.7, 129.0, 129.5, 129.8, 130.0, 132.4, 133.5, 146.7, 148.2, 149.6, 150.1, 175.4. HRMS (FAB) calcd for M^+ of $C_{30}H_{27}NO_3$ 449.1991, found 449.1991.



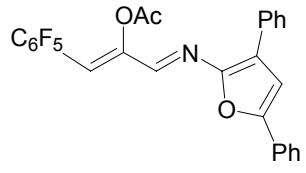
***N*-(2-Benzoyloxy-3-phenyl-2-propen-1-ylidene)-3,5-diphenyl-2-furanamine (3c)**: A yellow solid; mp 224.2-225.0 °C. IR (KBr): 690, 759, 1061, 1244, 1450, 1492, 1733 (C=O), 3426 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 6.78 (t, J = 7.6 Hz, 2H), 6.87 (s, 1H), 7.00 (t, J = 7.3 Hz, 2H), 7.30-7.36 (m, 4H), 7.41 (t, J = 7.6 Hz, 2H), 7.58-7.68 (m, 6H), 7.73-7.75 (m, 3H), 8.34 (d, J = 7.3 Hz, 2H), 8.45 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 107.1, 122.6, 124.1, 126.9, 127.6, 127.9, 128.1, 128.7, 128.8, 129.1, 129.2, 129.5, 129.7, 130.0, 130.6, 130.6, 131.8, 133.6, 133.7, 145.8, 146.8, 149.1, 150.4, 164.0. Anal. calcd for $C_{32}H_{23}NO_3$: C, 81.86; H, 4.94. Found: C, 81.89; H, 4.82.



***N*-[2-Acetoxy-3-(4-bromophenyl)-2-propen-1-ylidene]-3,5-diphenyl-2-furanamine (3d)**: A yellow solid; mp 222.0-223.4 °C. IR (KBr): 686, 755, 1215, 1488, 1636, 1750 (C=O), 3421 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 6.66 (s, 1H), 7.01 (s, 1H), 7.30-7.50 (m, 10H), 7.73 (d, J = 7.2 Hz, 2H), 7.82 (d, J = 7.2 Hz, 2H), 8.31 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0, 107.5, 123.2, 123.4, 124.0, 127.3, 127.4, 128.0, 128.1, 128.2, 128.7, 128.8, 130.8, 131.9, 132.3, 132.4, 145.7, 147.0, 148.9, 150.5, 167.9. HRMS (FAB) calcd for M^+ of $C_{27}H_{20}BrNO_3$ 487.0610, found 487.0629.

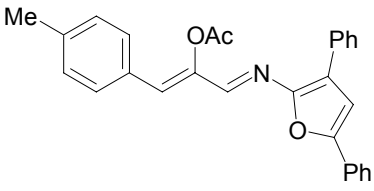


***N*-[2-Acetoxy-3-(4-trifluoromethylphenyl)-2-propen-1-ylidene]-3,5-diphenyl-2-furanamine (3e)**: A yellow solid; mp 174.5-175.5 °C. IR (KBr): 686, 755, 1069, 1113, 1165, 1328, 1612, 1751 (C=O), 3448 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 6.71 (s, 1H), 6.99 (s, 1H), 7.30-7.31 (m, 2H), 7.37-7.43 (m, 4H), 7.60 (d, J = 8.4 Hz, 2H), 7.64-7.71 (m, 4H), 7.82 (d, J = 7.2 Hz, 2H), 8.29 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0, 107.5, 123.9, 125.6 (q, J = 3.7 Hz), 125.8 (q, J = 272.5 Hz), 126.7, 127.9, 128.2, 128.4, 128.7, 128.9, 129.5, 129.8, 130.1, 130.4 (q, J = 32.9 Hz), 132.2, 136.8, 145.4, 148.2, 148.8, 150.8, 168.0. HRMS (FAB) calcd for M^+ of $C_{28}H_{20}F_3NO_3$ 475.1395, found 475.1389.

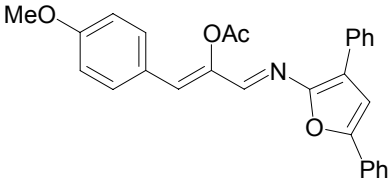


***N*-[2-Acetoxy-3-(1,2,3,4,5-pentafluorophenyl)-2-propen-1-ylidene]-3,5-diphenyl-2-furanamine (3f)**: A yellow solid; mp 222.8-223.9 °C. IR (KBr): 690, 758, 998, 1180, 1496, 1517, 1778 (C=O), 3448 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 3H), 6.61 (s, 1H), 7.04 (s, 1H), 7.30-7.46 (m, 6H), 7.75 (d, J = 7.2 Hz, 2H), 7.82 (d, J = 7.2 Hz, 2H), 8.37 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.7, 107.7, 108.4-108.9 (m), 111.4, 124.2, 125.2, 127.7, 128.2, 128.5, 128.7, 128.9, 129.7, 132.1, 137.8 (dm, J = 251.8 Hz), 141.1 (dm, J = 250.0 Hz), 144.0, 144.4 (dm, J = 246.2 Hz), 148.3, 150.9, 151.4, 167.9.

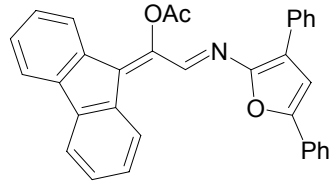
HRMS (FAB) calcd for M^+ of $C_{27}H_{16}F_5NO_3$ 497.1050, found 497.1043.



***N*-[2-Acetoxy-3-(4-methylphenyl)-2-propen-1-ylidene]-3,5-diphenyl-2-furanamine (3g)**: A yellow solid; mp 186.0-186.8 °C. IR (KBr): 692, 756, 861, 925, 1211, 1493, 1756 (C=O), 3448 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.38 (s, 3H), 2.42 (s, 3H), 6.73 (s, 1H), 7.02 (s, 1H), 7.19-7.32 (m, 4H), 7.39 (d, J = 8.1 Hz, 2H), 753 (d, J = 8.1 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 7.3 Hz, 2H), 7.85 (d, J = 7.3 Hz, 2H), 8.36 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0, 21.5, 107.4, 122.6, 124.0, 127.2, 128.0, 128.2, 128.7, 128.9, 129.1, 129.5, 129.6, 130.0, 130.8, 132.5, 139.5, 146.0, 146.4, 149.2, 150.3, 168.2. HRMS (FAB) calcd for M^+ of $C_{28}H_{23}NO_3$ 421.1678, found 421.1674.

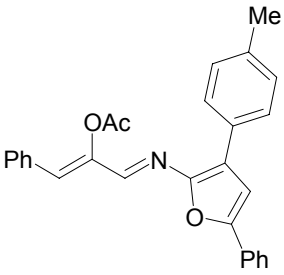


***N*-[2-Acetoxy-3-(4-methoxyphenyl)-2-propen-1-ylidene]-3,5-diphenyl-2-furanamine (3h)**: A yellow solid; mp 144.2-145.0 °C. IR (KBr): 692, 757, 1028, 1208, 1256, 1508, 1601, 1752 (C=O), 3422 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.43 (s, 3H), 3.85 (s, 3H), 6.70 (s, 1H), 6.92 (d, J = 8.7 Hz, 2H), 7.01 (s, 1H), 7.28-7.45 (m, 6H), 7.59 (d, J = 8.7 Hz, 2H), 7.73 (d, J = 7.8 Hz, 2H), 7.85 (d, J = 7.8 Hz, 2H), 8.34 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 55.4, 107.4, 114.3, 122.3, 123.9, 126.3, 127.1, 127.9, 127.9, 128.2, 128.7, 128.8, 130.0, 131.2, 132.5, 145.0, 146.4, 149.2, 150.1, 160.3, 168.2. HRMS (FAB) calcd for M^+ of $C_{28}H_{23}NO_4$ 437.1627, found 437.1625.

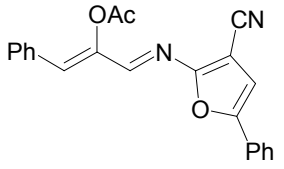


***N*-[2-Acetoxy-2-(9H-fluoren-9-ylidene)ethylidene]-3,5-diphenyl-2-furanamine (3i):** A red solid; 266.7-267.2 °C. λ_{abs} = 476 nm (ε = 2.6×10^{-6} L mol^{-1} cm^{-1}, 5.0×10^{-6} M in CH_2Cl_2), λ_{em} = 557 nm (λ_{ex} = 476 nm, 5.0×10^{-7} M in CH_2Cl_2). IR: (KBr) 688, 727, 758, 1017, 1200, 1369, 1444, 1474, 1490, 1759 (C=O), 3448 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 2.53 (s, 3H), 7.10 (s, 1H), 7.26-7.50 (m,

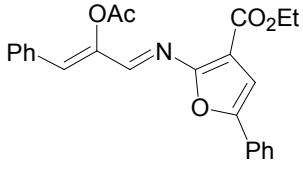
10H), 7.70-7.75 (m, 2H), 7.79 (d, J = 7.6 Hz, 2H), 7.89-7.97 (m, 4H), 9.33 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 108.2, 119.8, 120.3, 124.3, 125.5, 125.8, 126.2, 127.4, 127.7, 127.8, 128.2, 128.3, 128.5, 128.9, 129.0, 129.5, 129.7, 132.2, 134.1, 135.4, 137.0, 140.3, 141.2, 142.1, 146.0, 149.7, 151.6, 168.4. HRMS (FAB) calcd for M^+ of $C_{33}H_{23}NO_3$, 481.1678, found 487.1673.



***N*-(2-Acetoxy-3-phenyl-2-propen-1-ylidene)-3-(4-methylphenyl)-5-phenyl-2-furanamine (3j)**: A yellow solid; mp 202.0-203.5 ℃. IR (KBr): 689, 760, 809, 928, 1197, 1447, 1758 (C=O), 3448 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.39 (s, 3H), 2.44 (s, 3H), 6.74 (s, 1H), 7.00 (s, 1H), 7.20-7.43 (m, 8H), 7.63 (d, J = 6.6 Hz, 2H), 7.73-7.76 (m, 4H), 8.34 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 21.4, 107.4, 123.0, 124.0, 127.8, 128.0, 128.6, 128.6, 128.7, 128.8, 128.9, 129.0, 129.4, 130.0, 133.5, 137.1, 145.7, 146.6, 148.8, 150.3, 168.1. HRMS (FAB) calcd for M^+ of $C_{28}H_{23}NO_3$, 421.1678, found 421.1683.

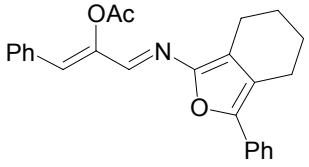


2-(2-Acetoxy-3-phenyl-2-propen-1-ylidene)amino-5-phenyl-3-furan carbonitrile (3k): A yellow solid; mp 156.2-157.1 ^{o}C. IR (KBr): 688, 755, 1205, 1449, 1599, 1752 (C=O), 3422 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.47 (s, 3H), 6.82 (s, 1H), 6.89 (s, 1H), 7.35-7.46 (m, 6H), 7.64-7.68 (m, 4H), 8.39 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.9, 94.1, 107.8, 113.2, 118.2, 124.3, 128.9, 129.0, 129.2, 130.1, 130.2, 132.9, 133.3, 145.7, 151.5, 152.7, 158.5, 168.4. HRMS (FAB) calcd for M^+ of $C_{22}H_{16}N_2O_3$ 357.1161, found 357.1169.

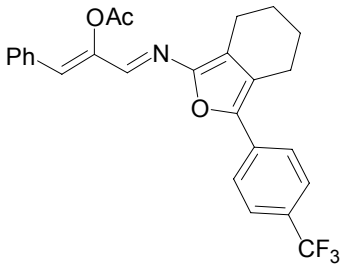


Ethyl 2-(2-acetoxy-3-phenyl-2-propen-1-ylidene)amino-5-phenyl-3-furancarboxylate (3l): A yellow solid; mp 122.1-123.1 ^{o}C. IR (KBr): 689, 758, 1200, 1484, 1589, 1692, 1758 (C=O), 3430 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.39 (t, J = 6.8 Hz, 3H), 2.50 (s, 3H), 4.35 (q, J = 6.8 Hz, 2H), 6.86 (s, 1H),

7.05 (s, 1H), 7.30-7.44 (m, 6H), 7.64-7.70 (m, 4H), 8.53 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.4, 21.0, 60.6, 108.5, 112.9, 124.0, 128.4, 128.8, 128.9, 129.4, 129.8, 129.9, 132.0, 133.1, 146.2, 149.8, 152.9, 154.7, 162.5, 168.5. HRMS (FAB) calcd for M^+ of $C_{24}H_{21}NO_5$ 403.1420, found 403.1428.

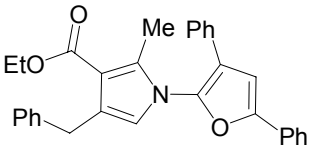


***N*-(2-Acetoxy-3-phenyl-2-propen-1-ylidene)-3-phenyl-4,5,6,7-tetrahydroisobenzofuran-1-amine (3m)**: A yellow solid; mp 84.2-85.1 ^{o}C. IR (KBr): 697, 758, 1202, 1449, 1493, 1691, 1754 (C=O), 2859, 2936, 3382 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.71-1.79 (m, 4H), 2.41 (s, 3H), 2.64 (t, J = 6.3 Hz, 2H), 2.76 (t, J = 6.3 Hz, 2H), 6.65 (s, 1H), 7.21-7.41 (m, 6H), 7.59 (d, J = 7.3 Hz, 2H), 7.64 (d, J = 7.3 Hz, 2H), 8.15 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.8, 20.9, 22.3, 22.9, 23.3, 122.0, 122.4, 124.7, 126.7, 127.2, 128.6, 128.7, 128.8, 129.4, 131.4, 133.7, 143.6, 144.1, 146.8, 148.0, 168.4. HRMS (FAB) calcd for M^+ of $C_{25}H_{23}NO_3$ 385.1678, found 385.1678.



***N*-(2-Acetoxy-3-phenyl-2-propen-1-ylidene)-3-(4-trifluoromethylphenyl)-4,5,6,7-tetrahydroisobenzofuran-1-amine (3n)**: A yellow solid; mp 150.2-150.9 ^{o}C. IR (KBr): 688, 754, 1205, 1325, 1609, 1760 (C=O), 2862, 2935, 3404 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.73-1.81 (m, 4H), 2.41 (s, 3H), 2.64 (t, J = 5.9 Hz, 2H), 2.76 (t, J = 5.9 Hz, 2H), 6.69 (s, 1H), 7.27-7.43 (m, 3H), 7.59-7.64 (m, 4H), 7.71 (d, J = 8.3 Hz, 2H), 8.18 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.7, 20.9, 22.2, 23.0, 23.1, 122.3, 124.1, 124.2 (q, J = 271 Hz), 124.4, 125.5 (q, J = 4.1 Hz), 128.1, 128.7, 128.8 (q, J = 67.0 Hz), 129.0, 129.5, 133.5, 134.6, 142.6, 145.0, 146.6, 148.8, 168.4. HRMS (FAB) calcd for M^+ of $C_{26}H_{22}F_3NO_3$ 453.1552, found 453.1560.

Synthetic of Ethyl *N*-[2-(3,5-Diphenylfuryl)]-2-methyl-4-benzylpyrrole-3-carboxylate (5). A



solution of *N*-(2-acetoxy-3-phenyl-2-propen-1-ylidene)-3,5-diphenyl-2-furanamine **3a** (40.7 mg, 0.10 mmol) in THF (2 mL) was added to $LiAlH_4$ (11.4 mg, 0.30 mmol) at 0 ^oC, and the resulting mixture was stirred for 2 h at rt. The obtained dark green solution was carefully poured into water (10 mL), and extracted with Et_2O (10 mL×3). The combined organic layer was dried over Na_2SO_4, then the organic solvent was removed under reduced pressure. The residue was passed through short silica gel pad, and concentrated in vacuo to give *N*-(3-phenyl-2-oxopropyl)-3,5-diphenyl-2-furanamine **4** (32.2 mg, 0.088 mmol, 88% yield) as a yellow viscous oil. IR (neat): 698, 765, 947, 1177, 1212, 1449, 1495, 1700, 1732 (C=O), 2851, 2923, 3025, 3062 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 3.78 (s, 2H), 4.28 (d, J = 5.2 Hz, 2H), 5.02 (t, J = 5.2 Hz, 1H), 6.78 (s, 1H), 7.13-7.50 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 47.4, 53.1, 102.3, 107.1, 122.2, 125.4, 125.9, 127.4, 128.6, 128.9, 129.0, 129.3, 129.4, 130.8, 133.1, 133.7, 144.9, 150.8, 204.0. HRMS (FAB) calcd for $M+H^+$ of $C_{25}H_{20}NO_2$ 368.1651, found 368.1659. To a solution of **4** (29.3 mg, 0.080 mmol), ethyl acetoacetate (21.0 mg, 0.16 mmol) in EtOH (2 mL) was added to sodium ethoxide (10.9 mg, 0.16 mmol), and the resulting mixture was stirred at 50 ^oC for 24 h. The reaction mixture was quenched by adding excess of 10% NH_4Cl aqueous solution, and the aqueous layer was extracted with Et_2O (10 mL×3). The combined organic layer was washed with brine and dried over $MgSO_4$. The organic solvent was removed under reduced pressure and the residue was subjected to flash column chromatography on silica gel with hexane/AcOEt (v/v = 20/1) as eluents to afford *N*-[2-(3,5-diphenylfuryl)]-2-methyl-4-benzylpyrrole-3-carboxylate **5** (27.0 mg, 0.060 mmol, 74% yield) as a yellow viscous oil. IR (neat): 694, 760, 801, 1027, 1095, 1261, 1420, 1637, 1700, 2925, 2963, 3027, 3060, 3384 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.27 (t, J = 7.3 H z, 3H), 2.34 (s, 3H), 4.10 (s, 2H), 4.25 (q, J = 7.3 Hz, 2H), 6.33 (s, 1H), 7.01 (s, 1H), 7.11-7.14 (m, 2H), 7.24-7.30 (m, 5H), 7.39-7.34 (m, 4H), 7.41 (t, J = 7.3 Hz, 2H), 7.69 (d, J = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.1, 14.3, 33.1, 59.5, 105.3, 112.8, 120.7, 120.8, 123.9, 125.7, 126.1, 126.2, 127.6, 128.1, 128.2, 128.7, 128.8, 128.9,

129.7, 130.5, 139.0, 139.1, 141.2, 151.3, 165.6. HRMS (FAB) calcd for $M+H^+$ of $C_{31}H_{27}NO_3$ 462.2069, found 462.2067.

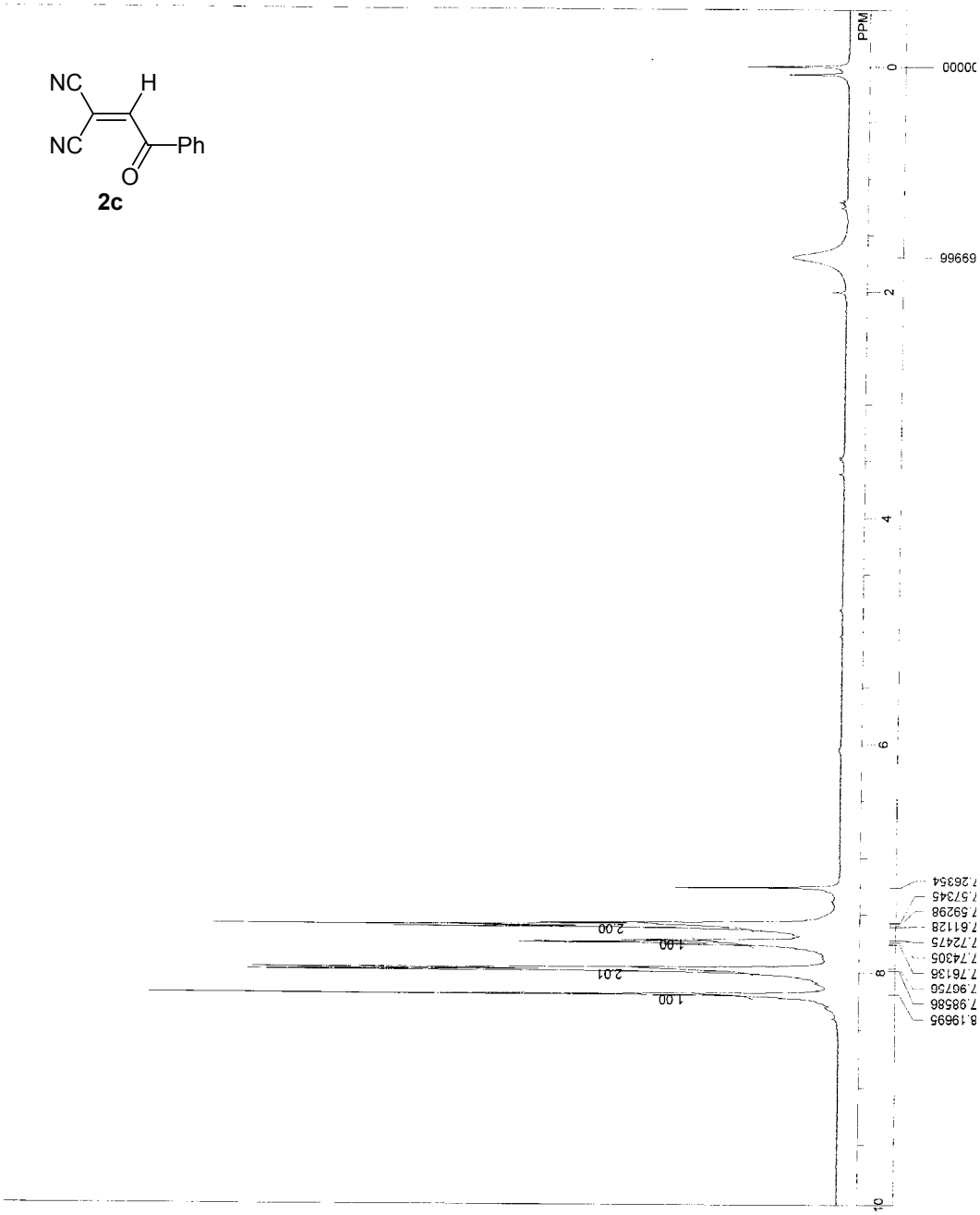
References

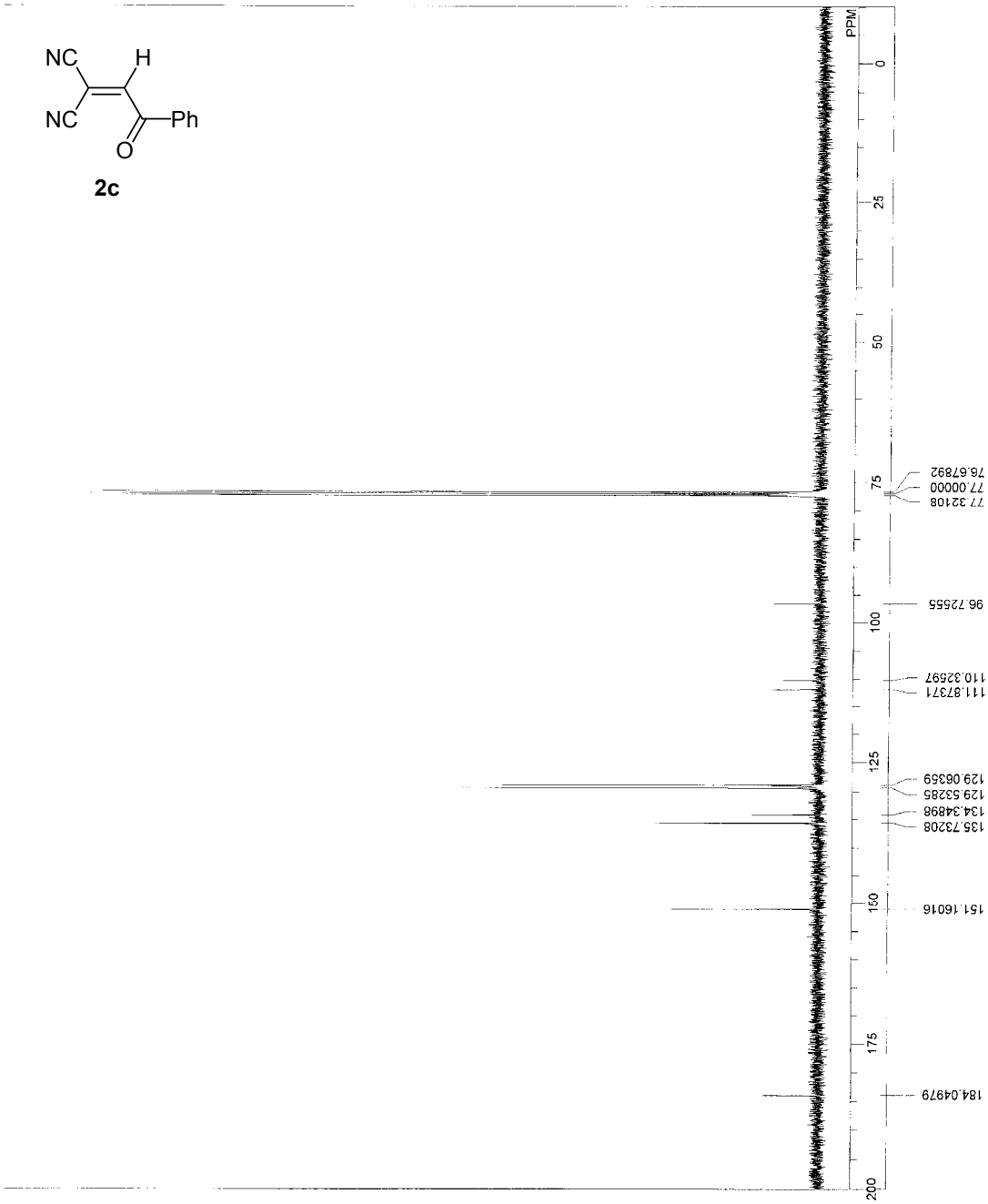
1 (a) K. Nozaki; N. Sato; H. Takaya, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1629; (b) M. Murai; K. Miki; K. Ohe, *J. Org. Chem.* **2008**, *73*, 9174.

2 (a) K. Miki; K. Ohe; S. Uemura, *J. Org. Chem.* **2003**, *68*, 8505; (b) Y. Nakanishi; K. Miki; K. Ohe, *Tetrahedron* **2007**, *63*, 12138.

3 B. Qin; X. Liu; J. Shi; K. Zheng; H. Zhao; X. Feng, *J. Org. Chem.* **2007**, *72*, 2374.

^{1}H NMR and ^{13}C NMR Spectra of Selected Compounds

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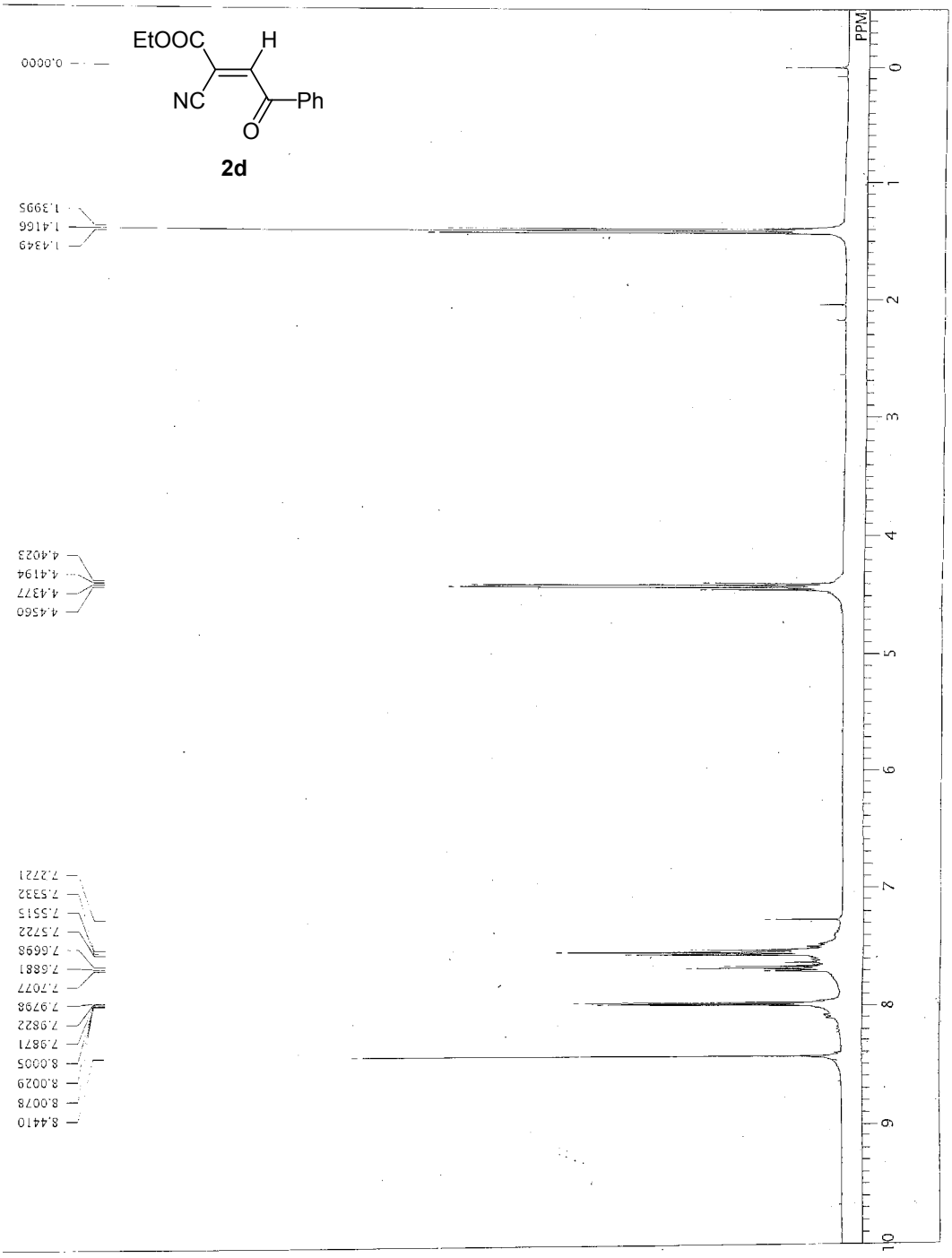
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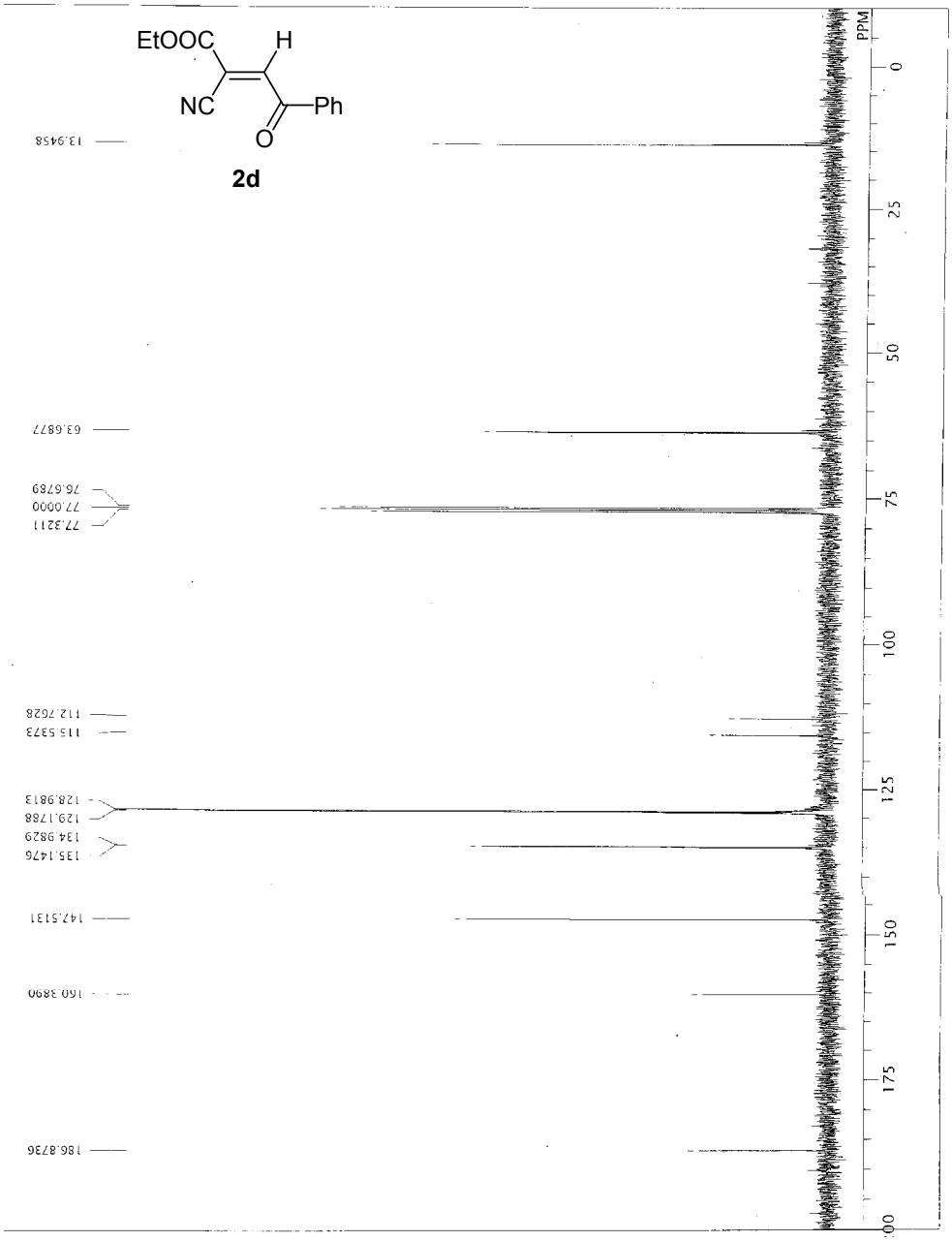
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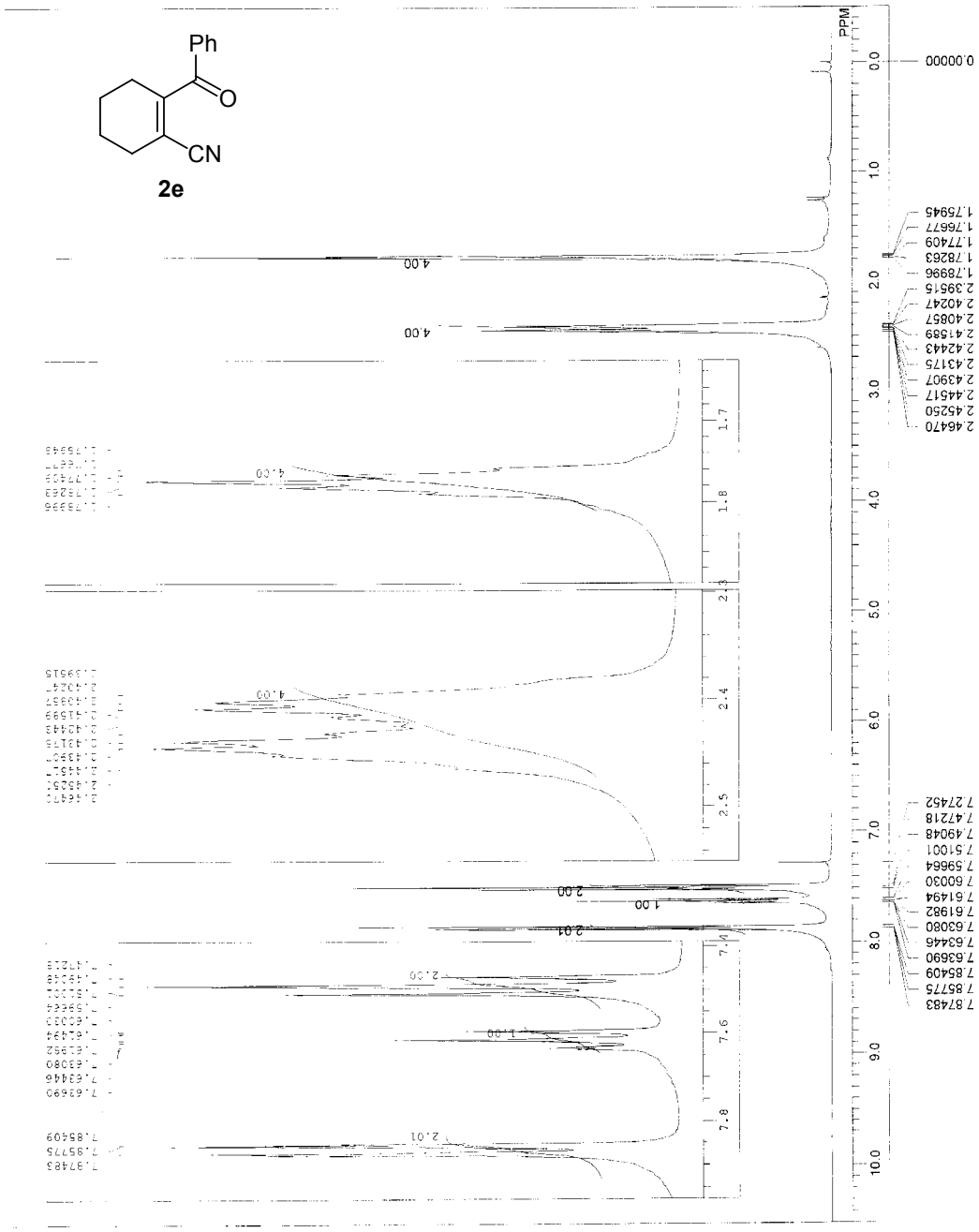
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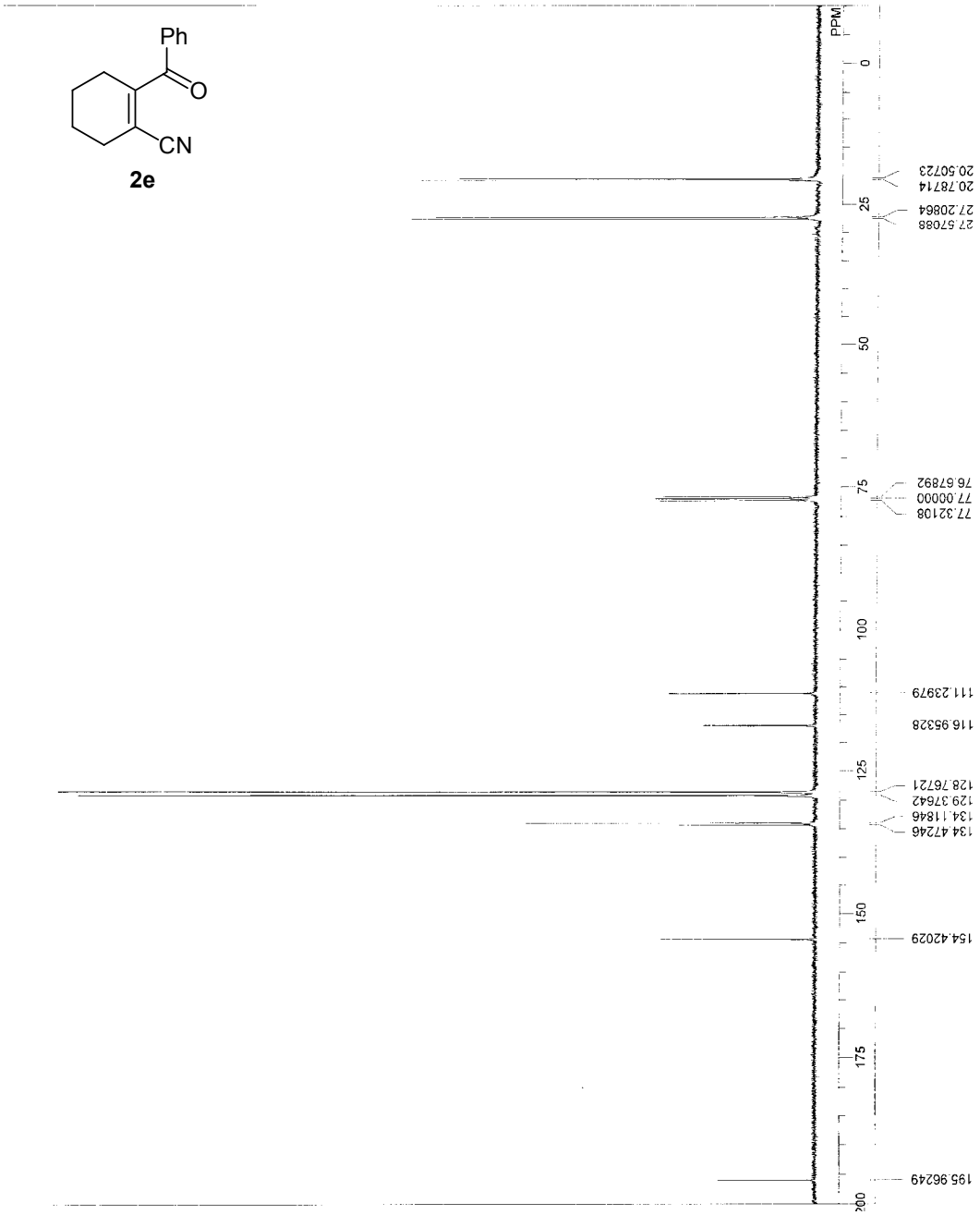
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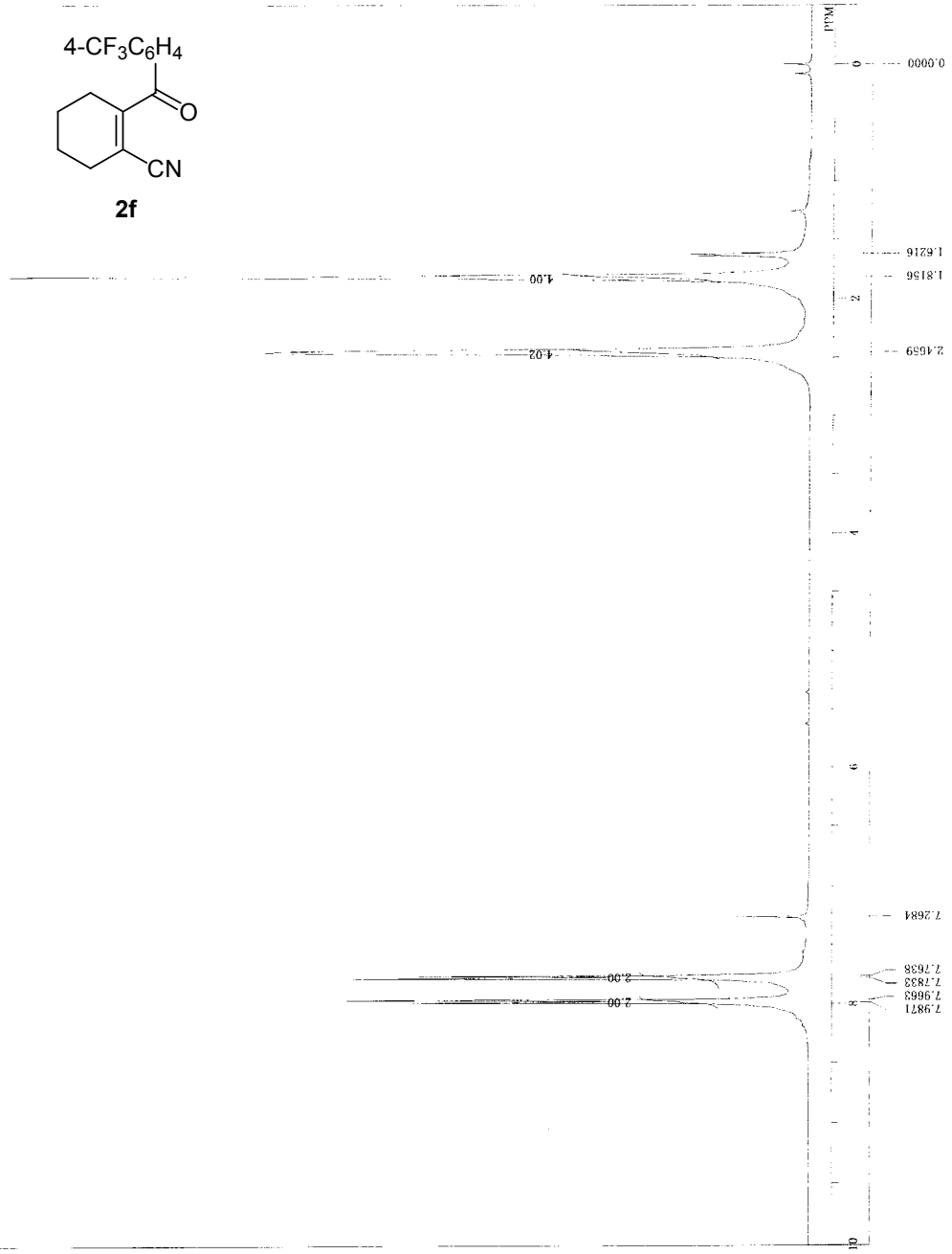
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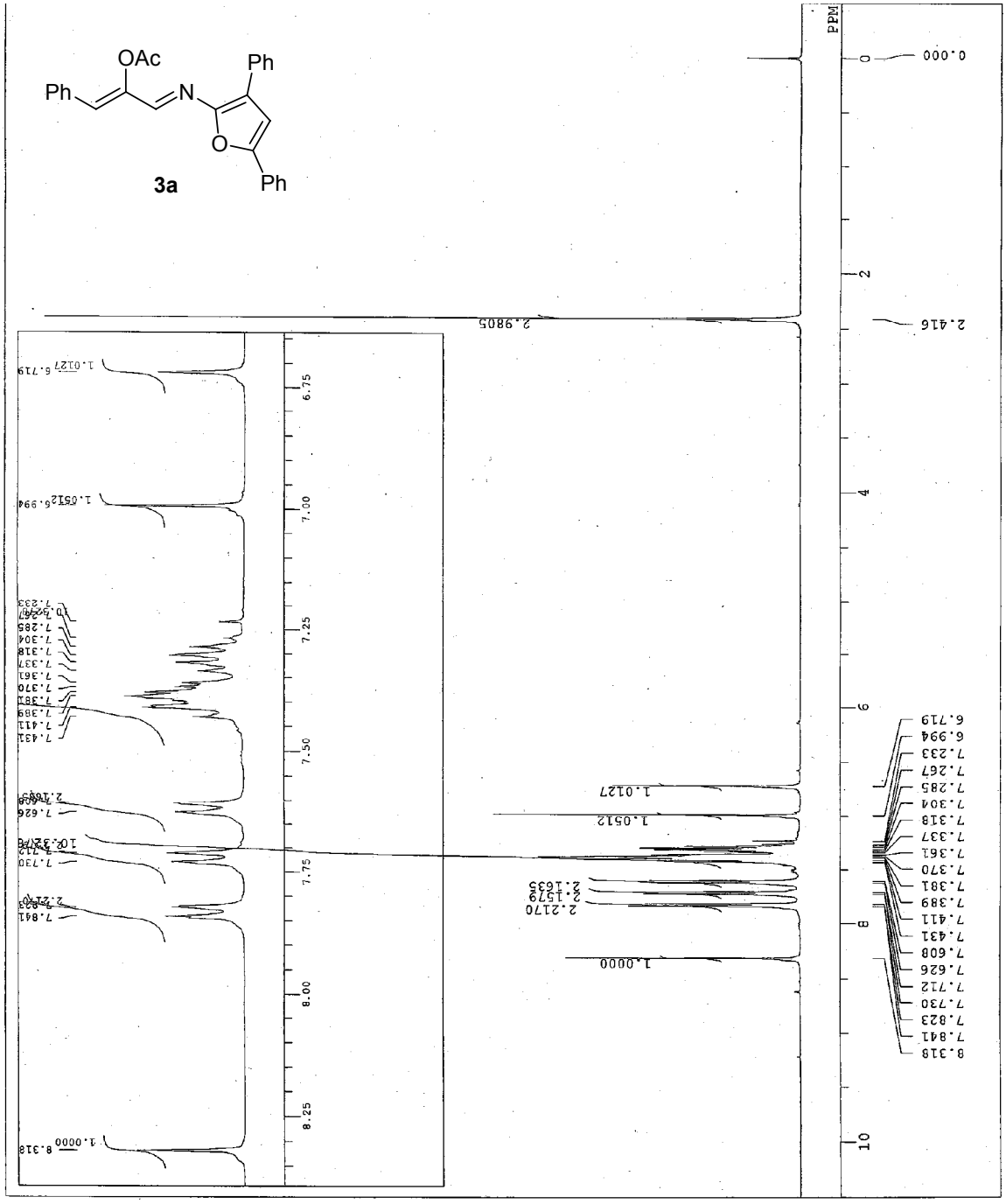
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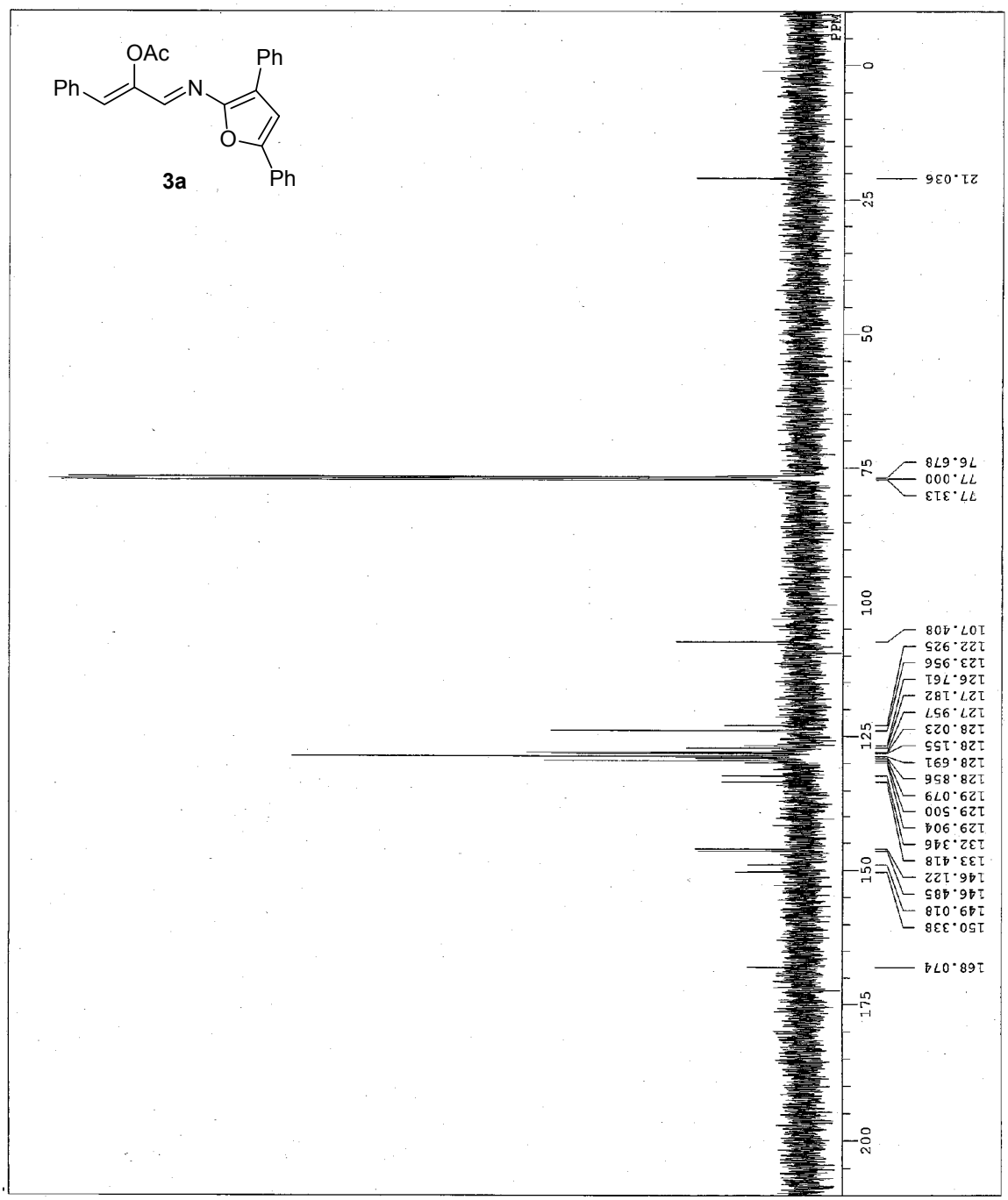
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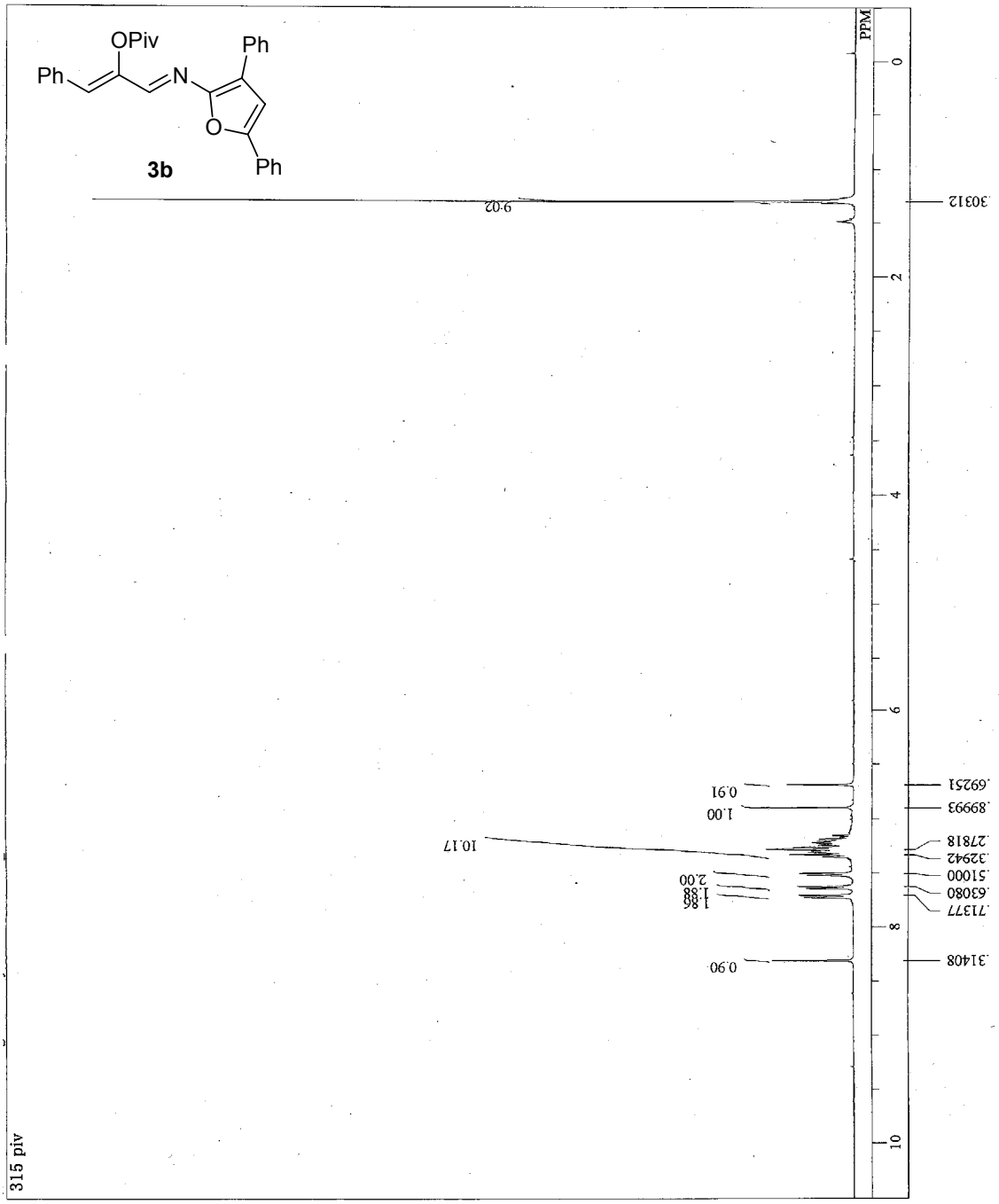
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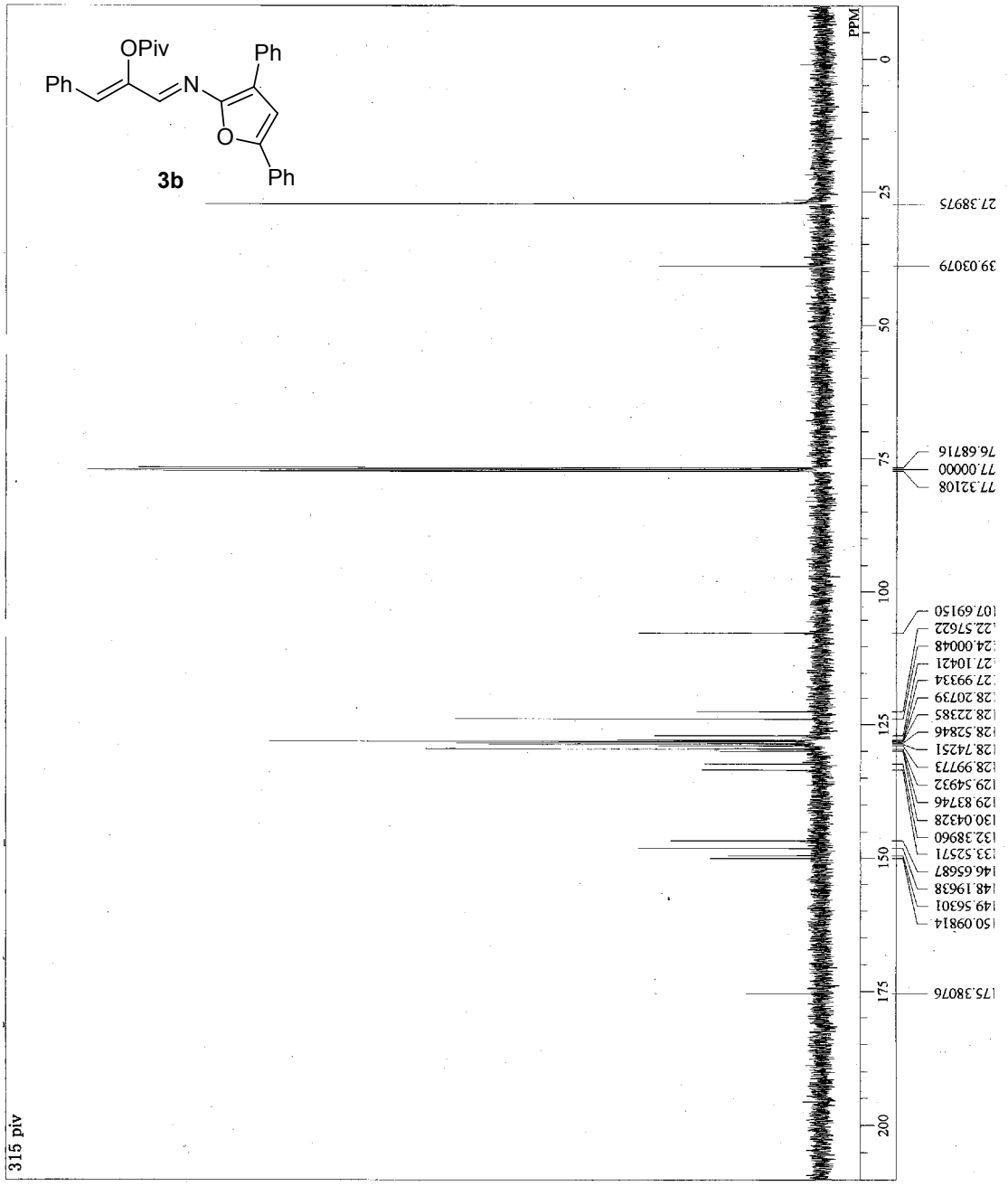
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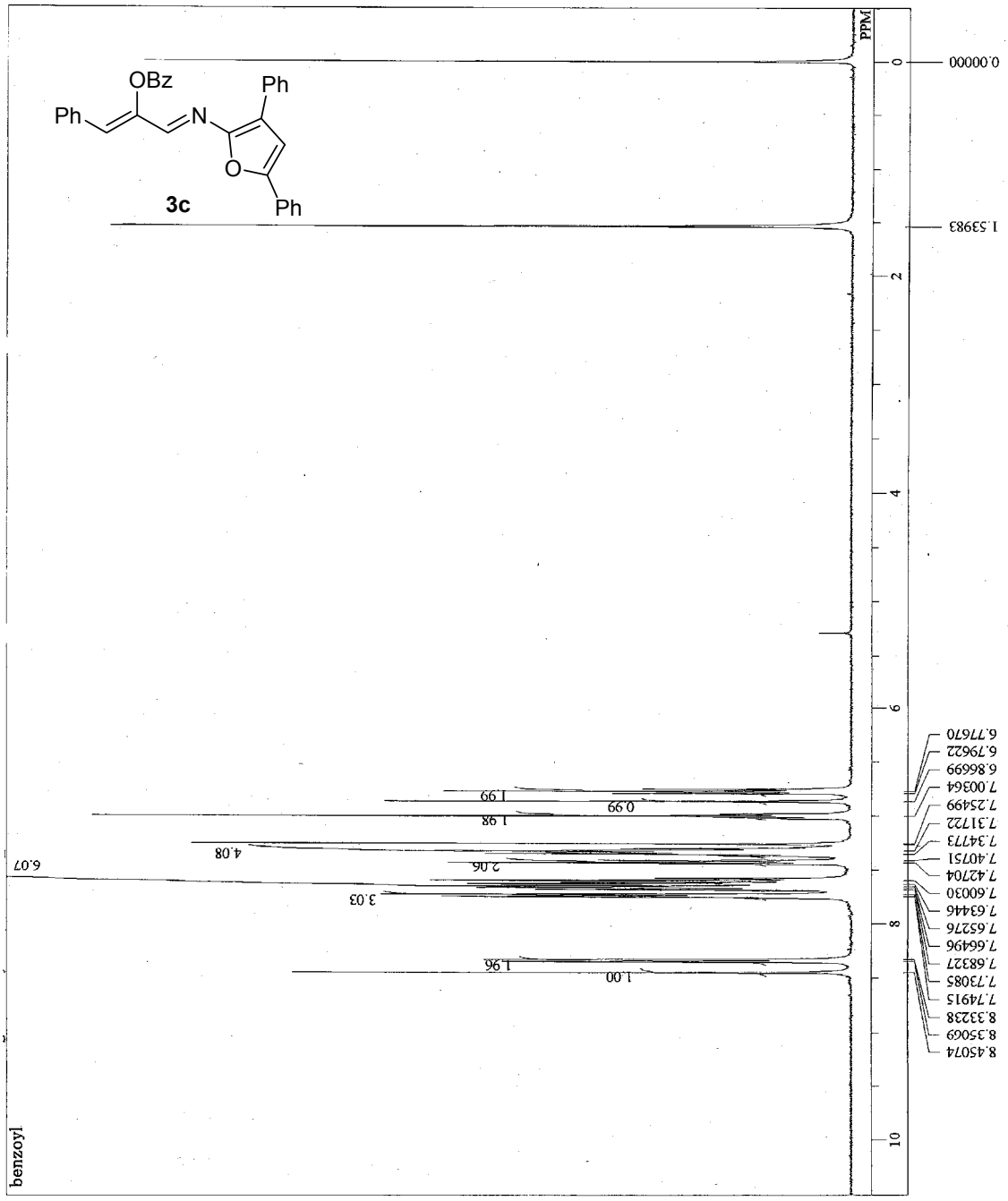
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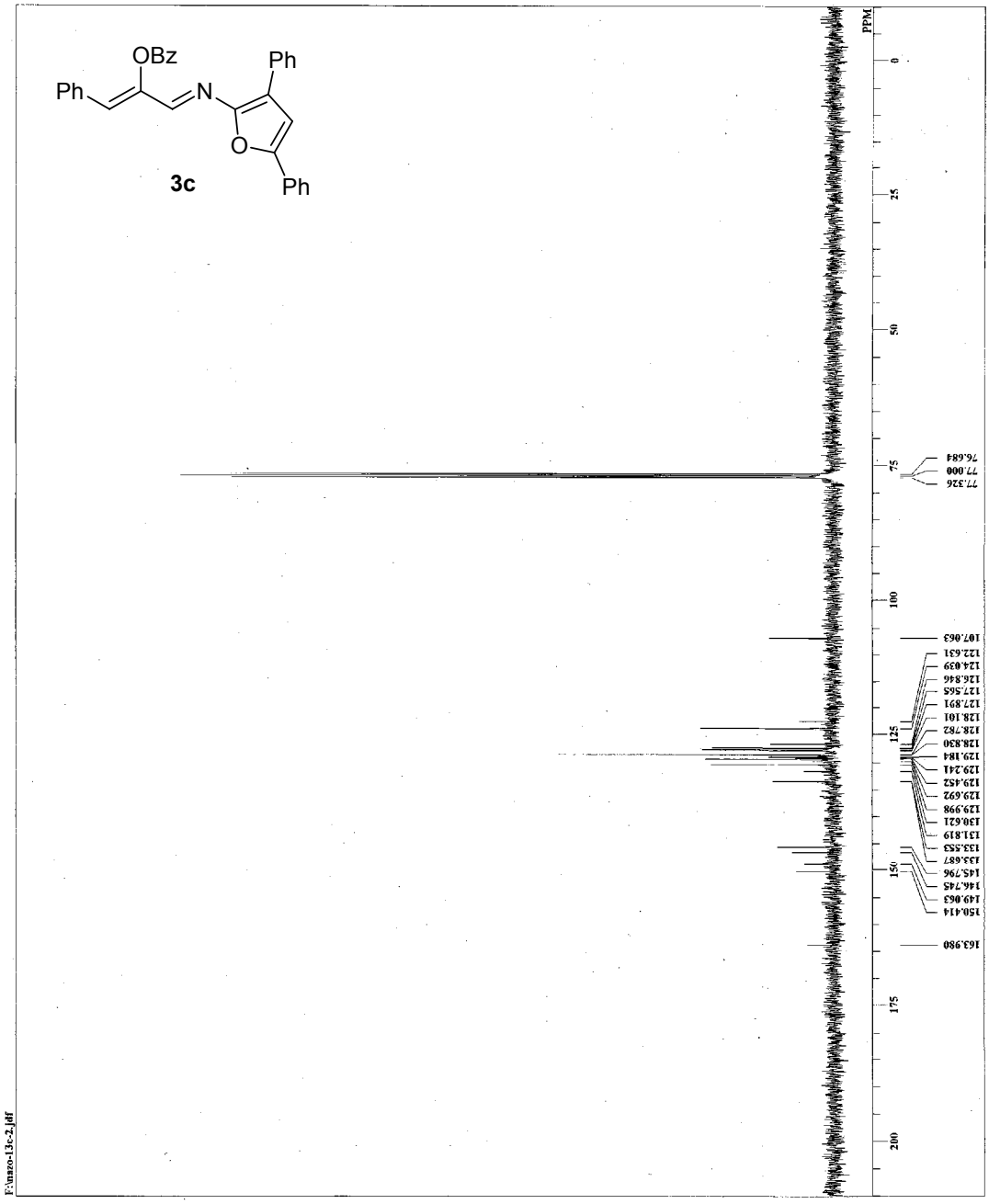
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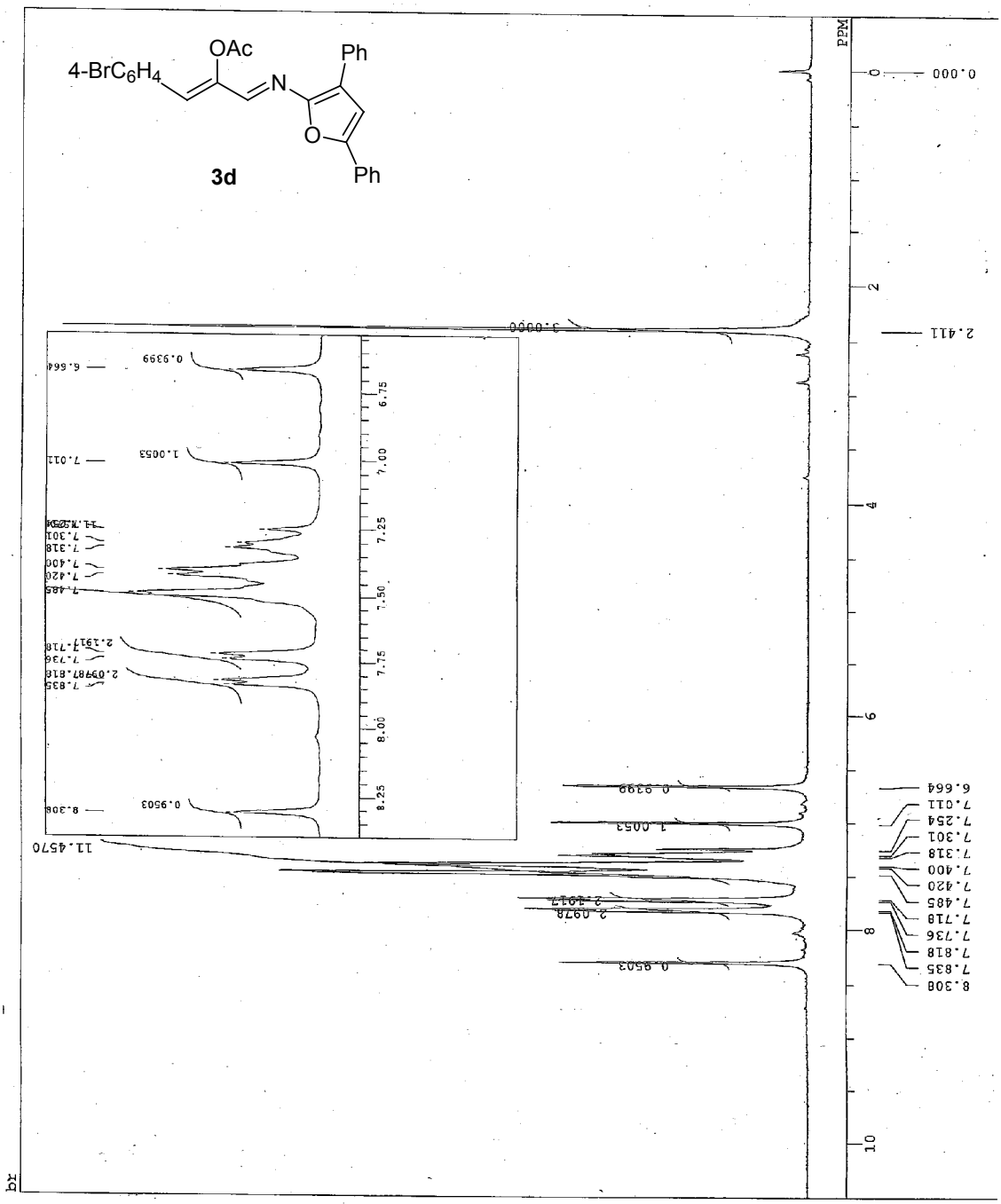
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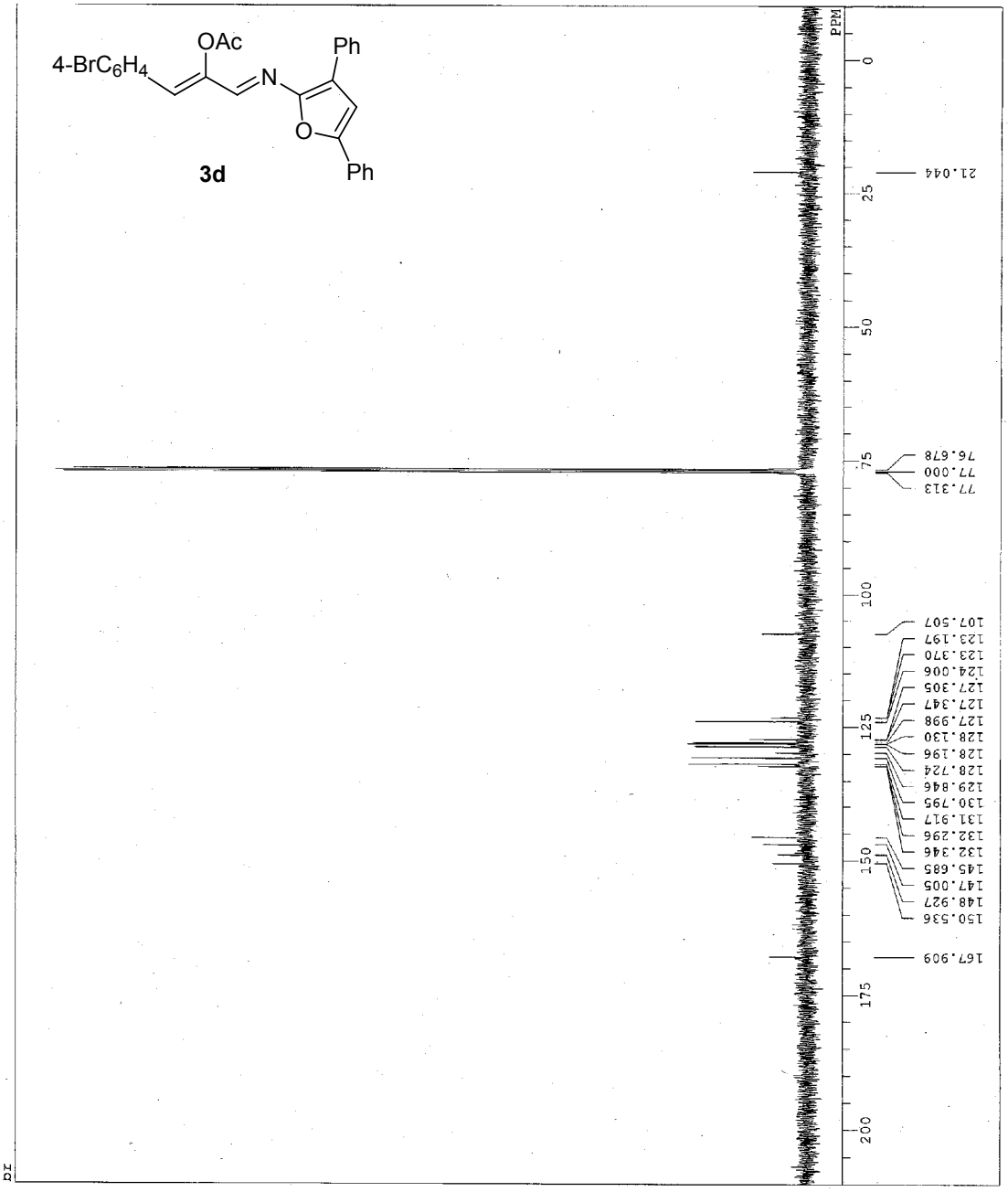
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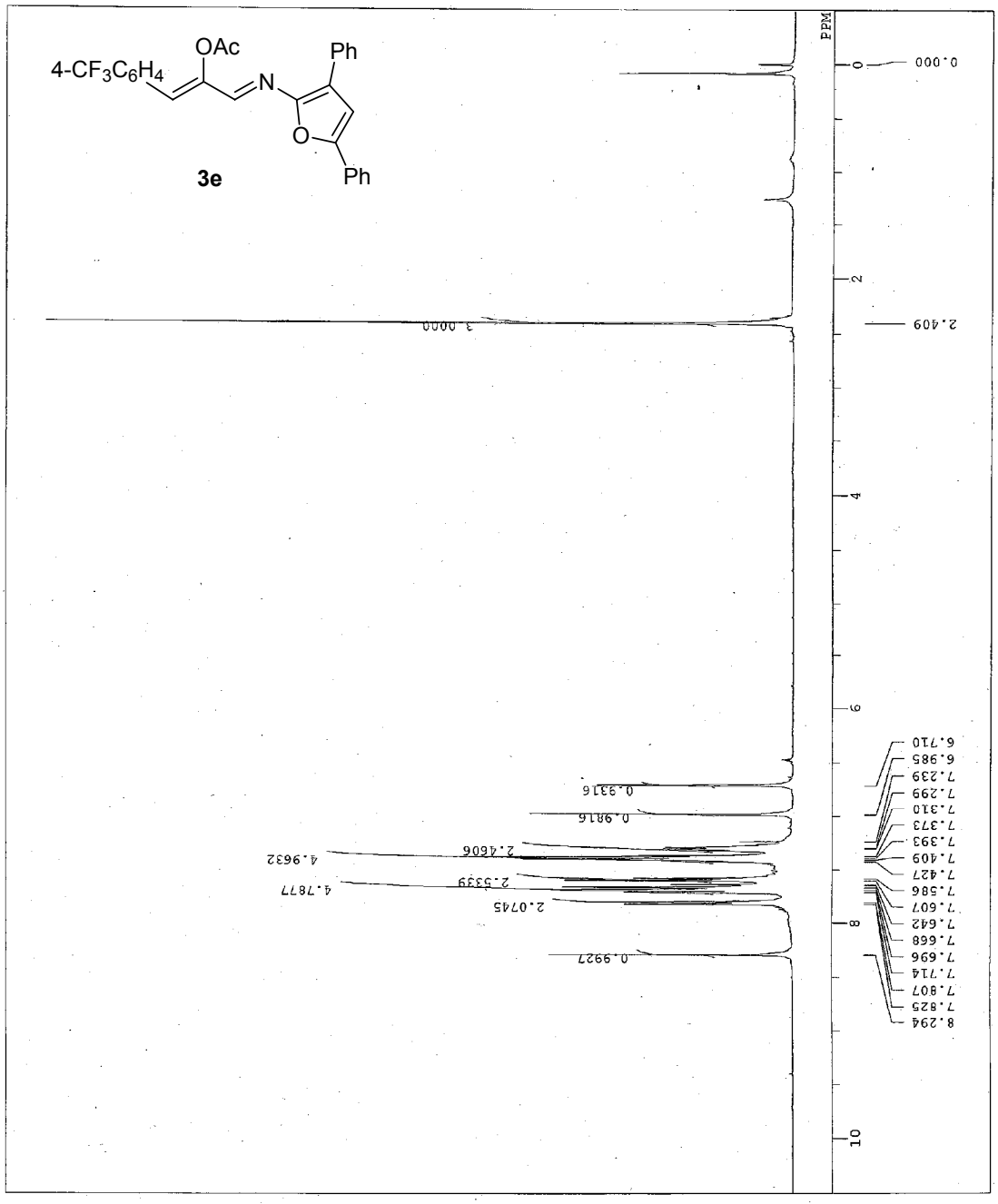
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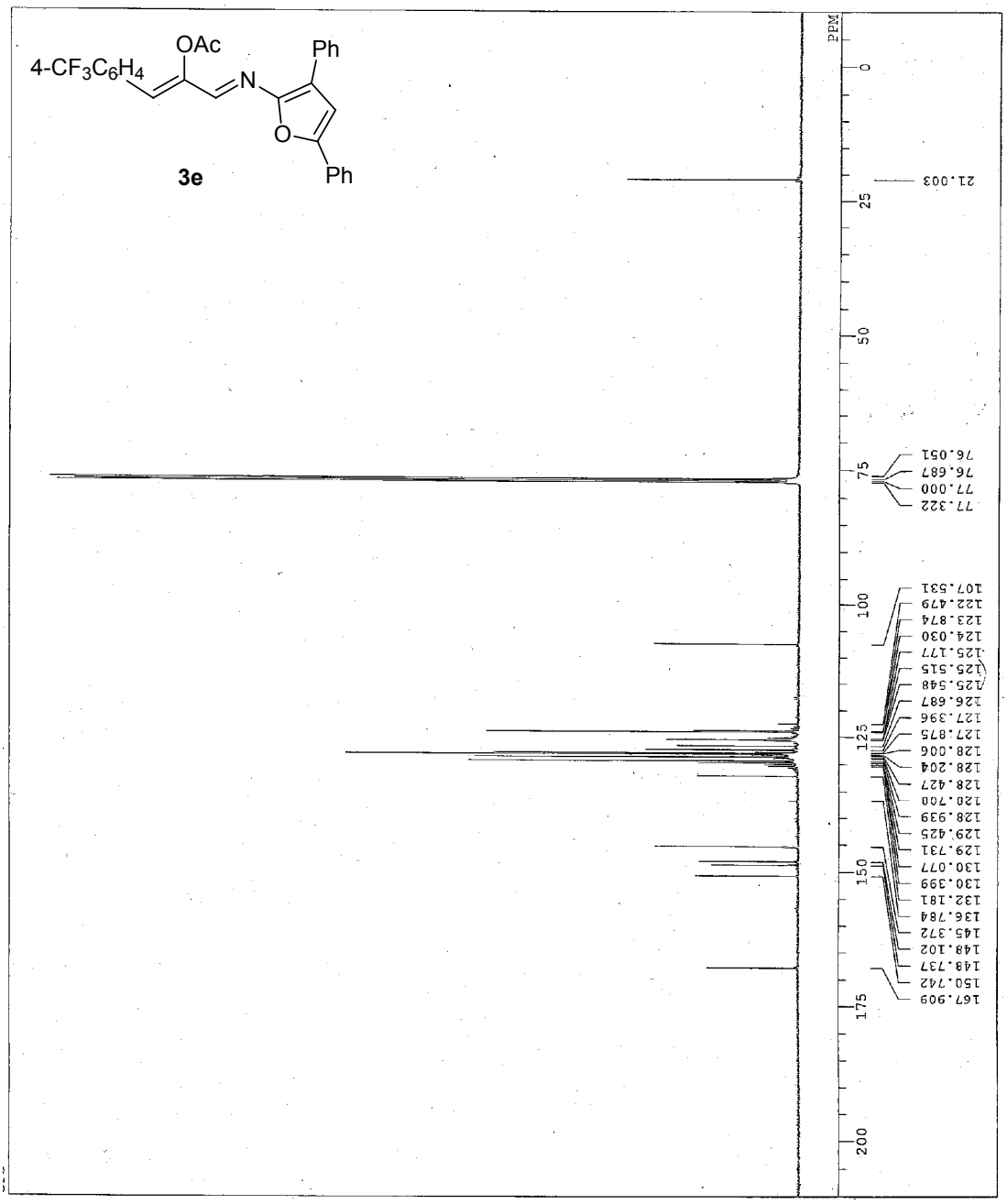
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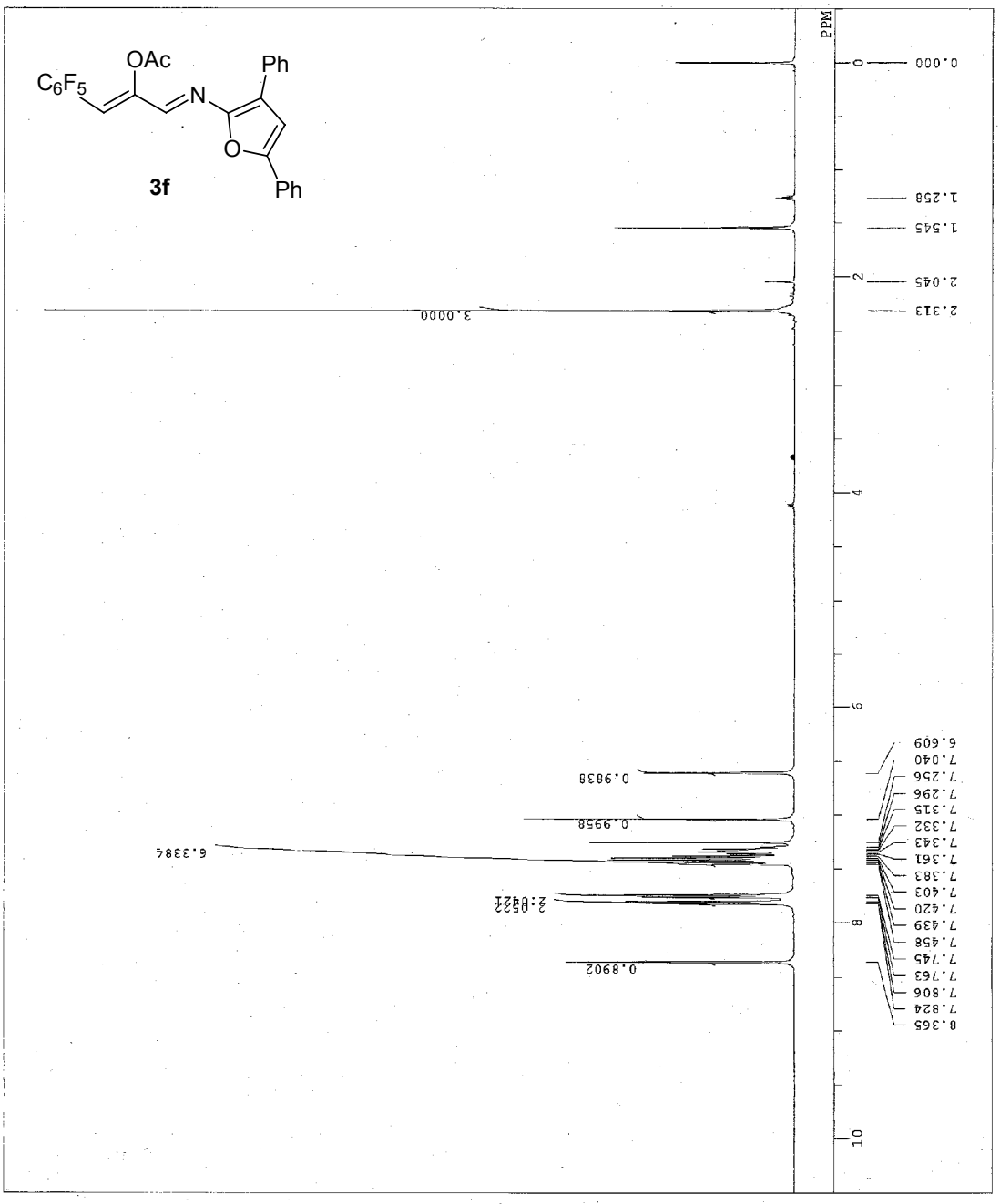
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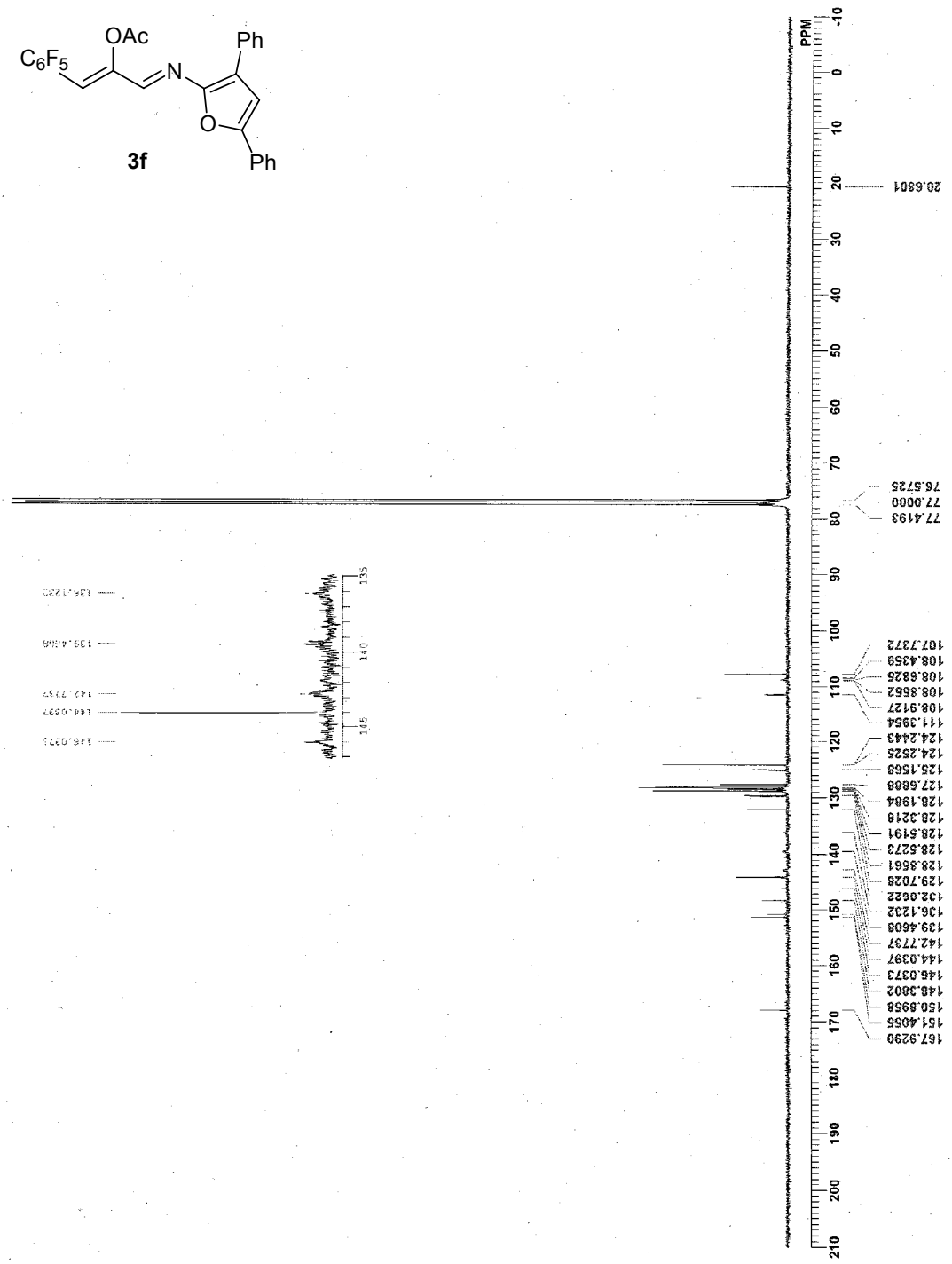
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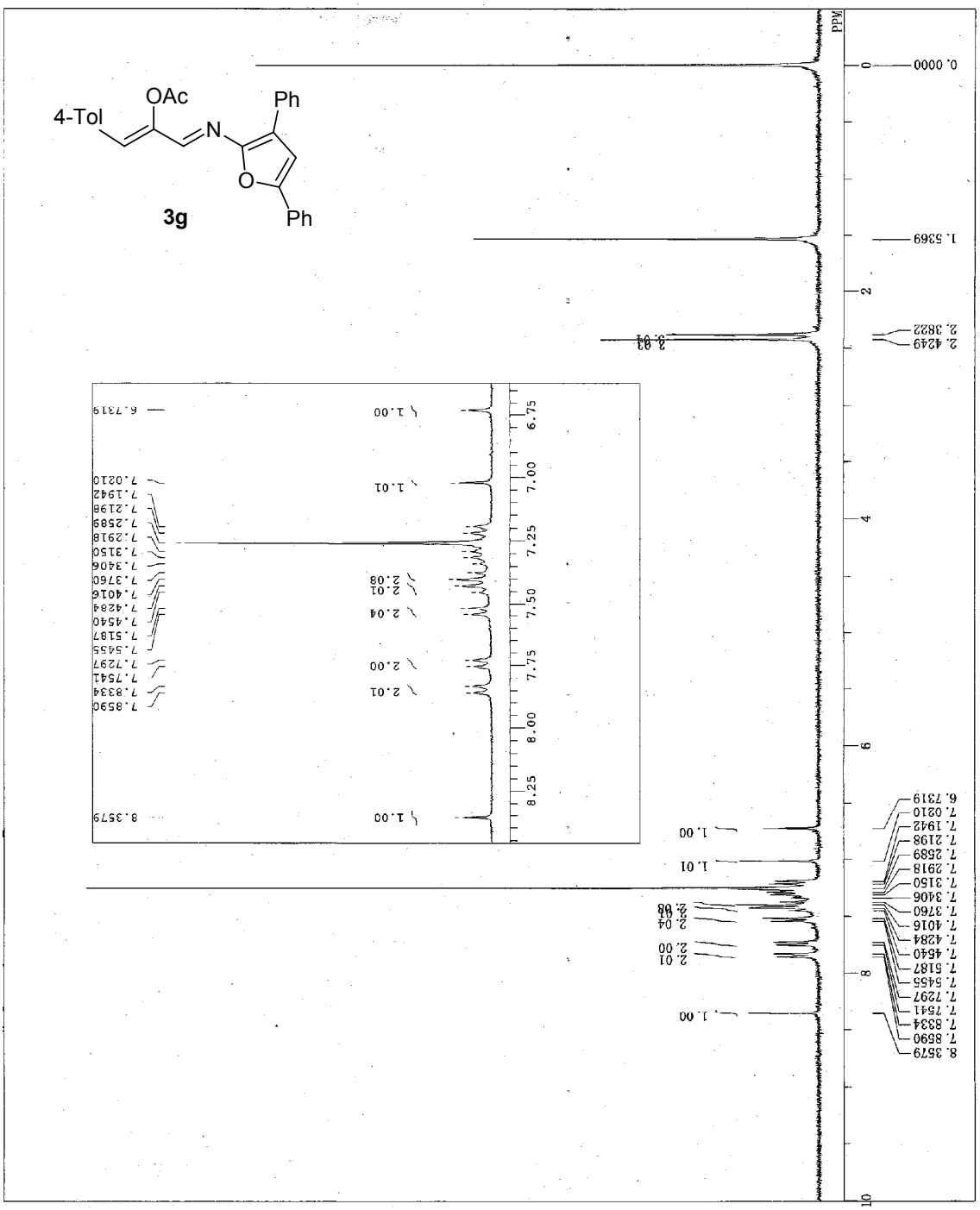
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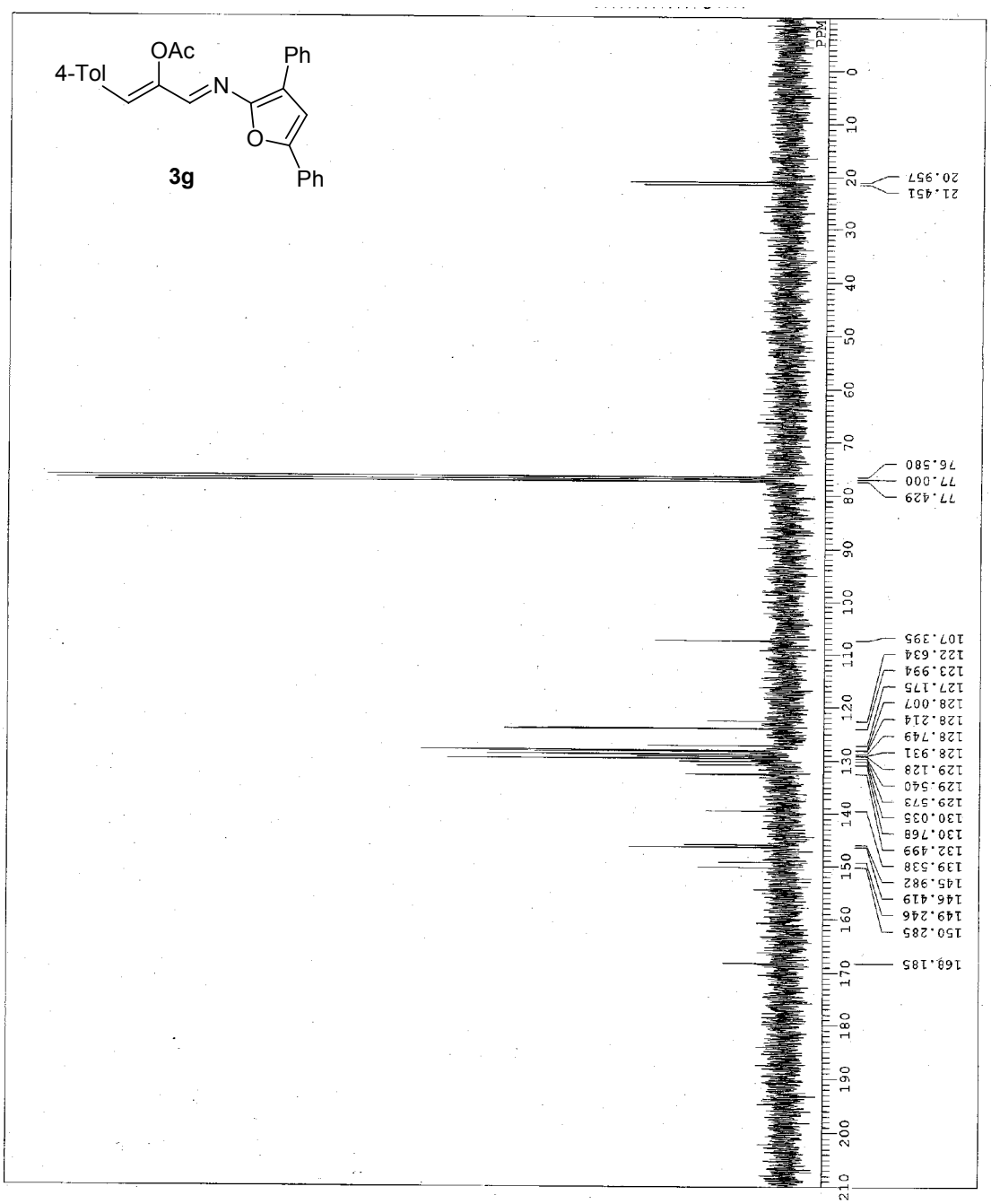
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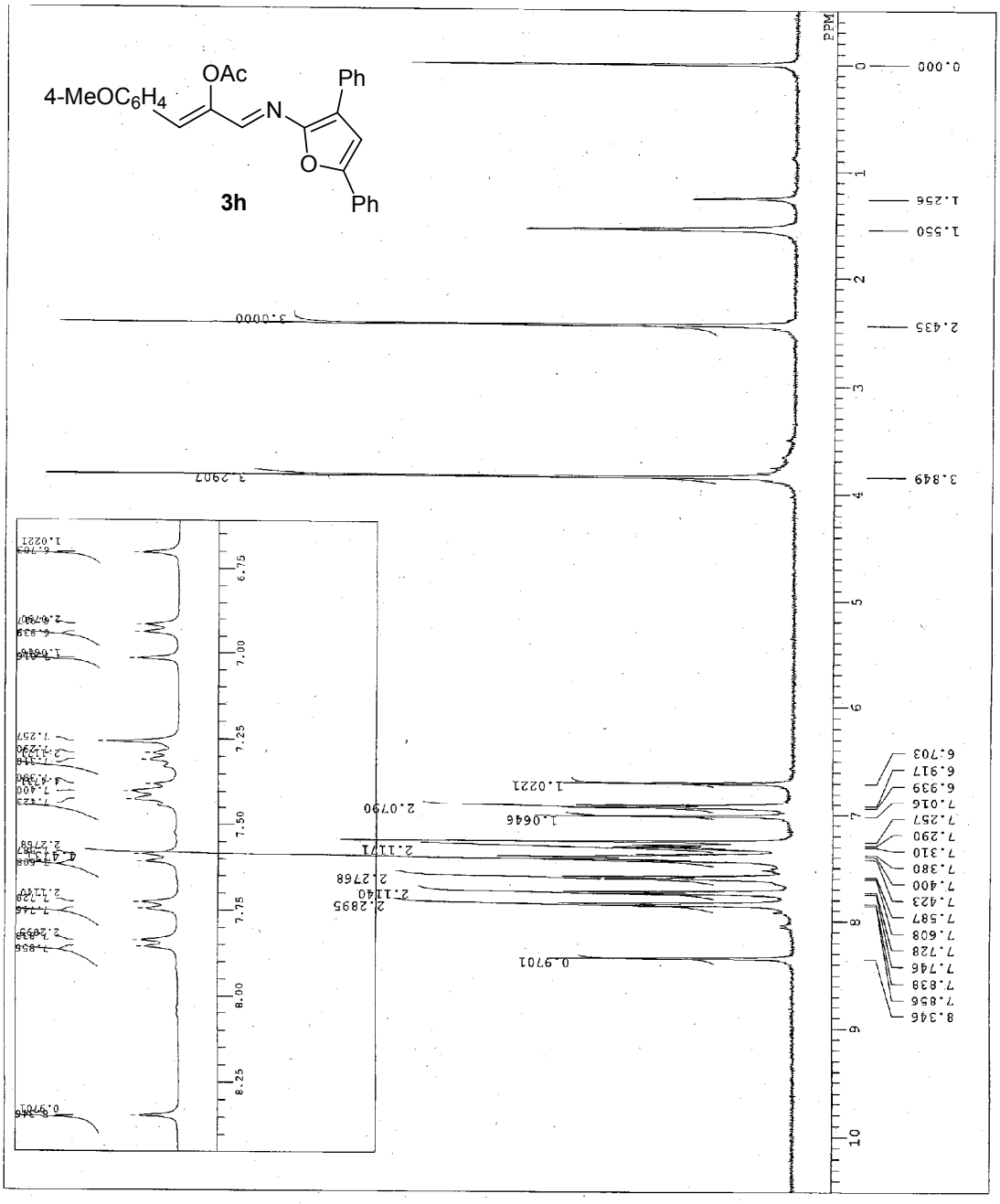
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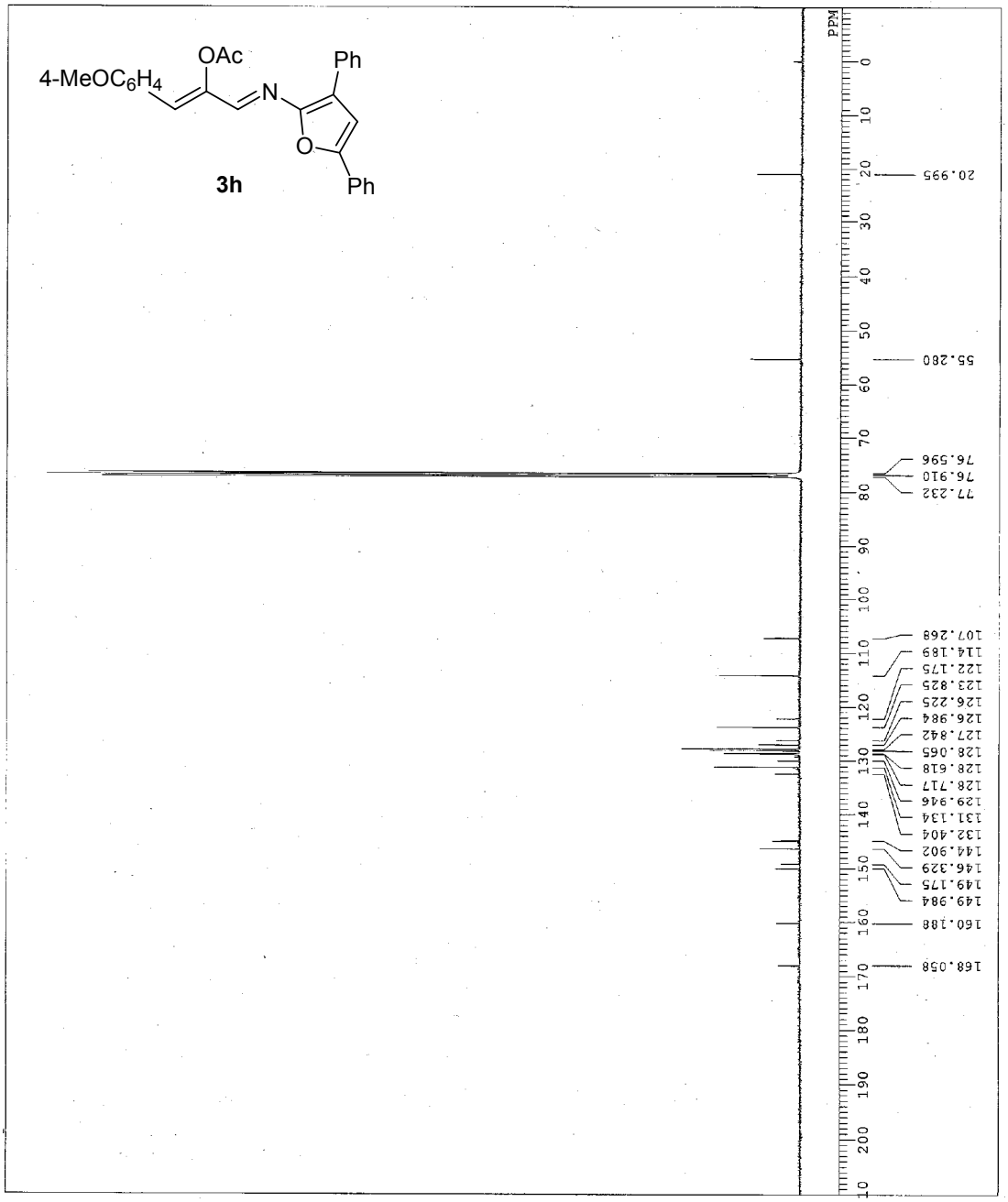
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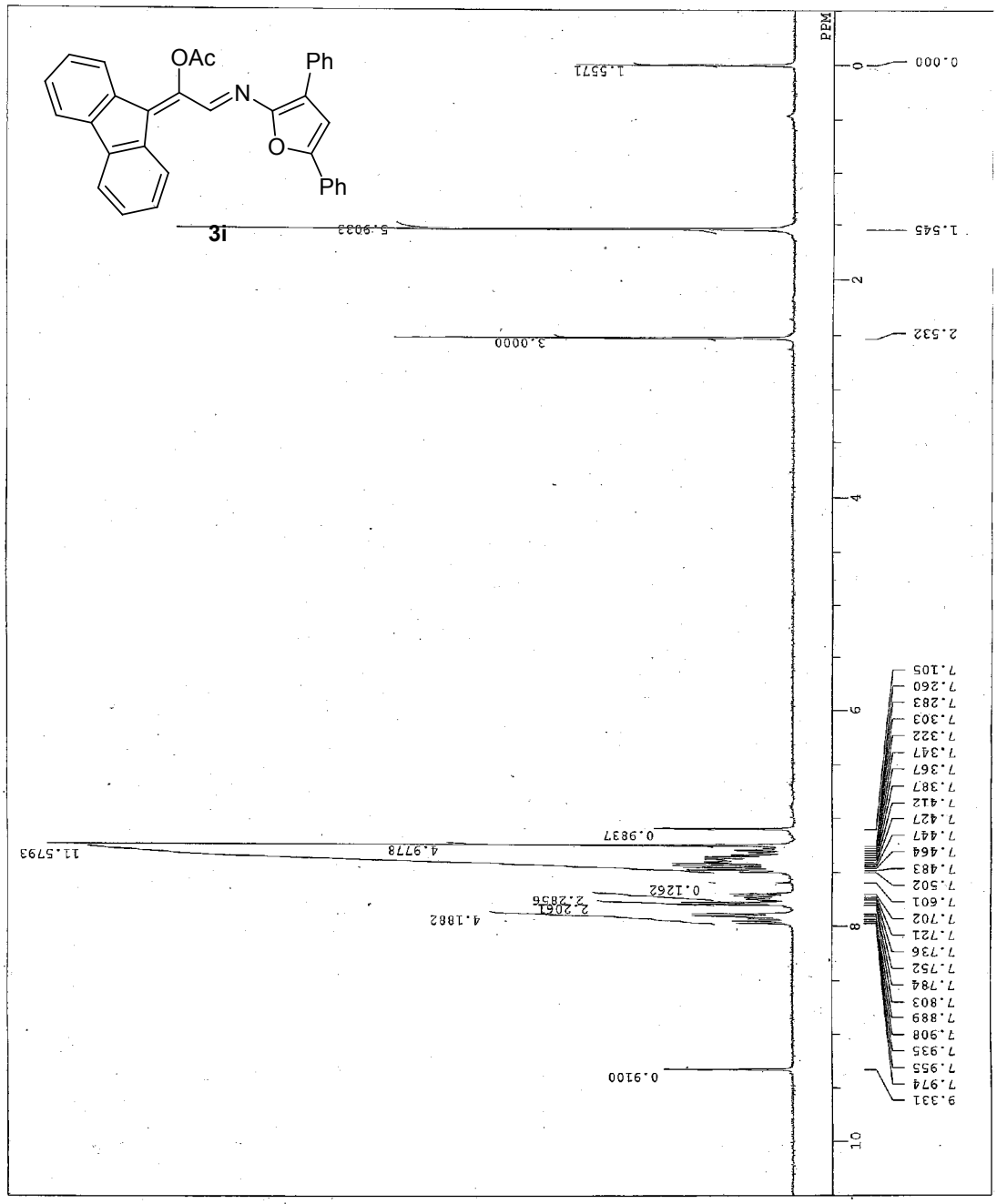
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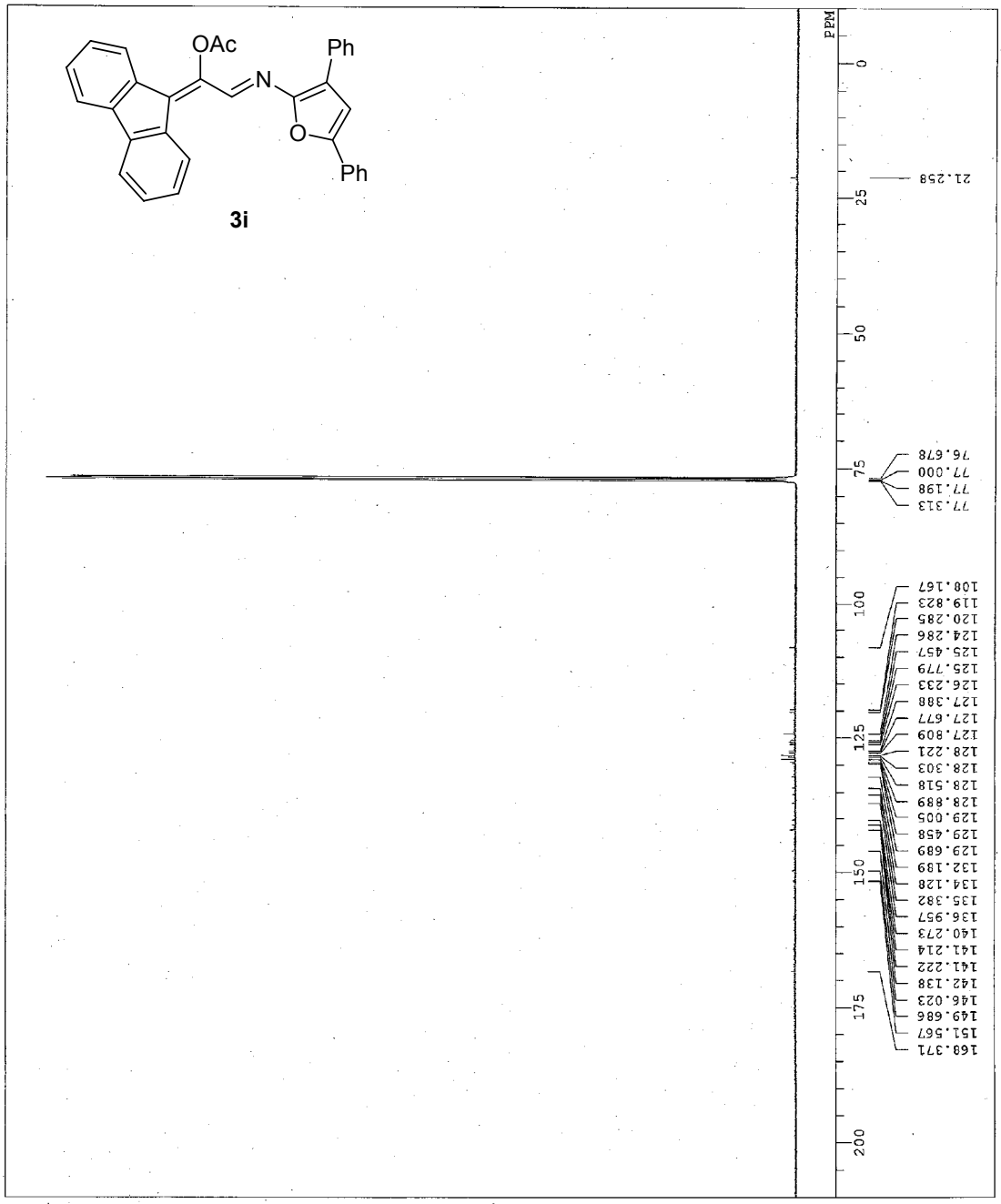
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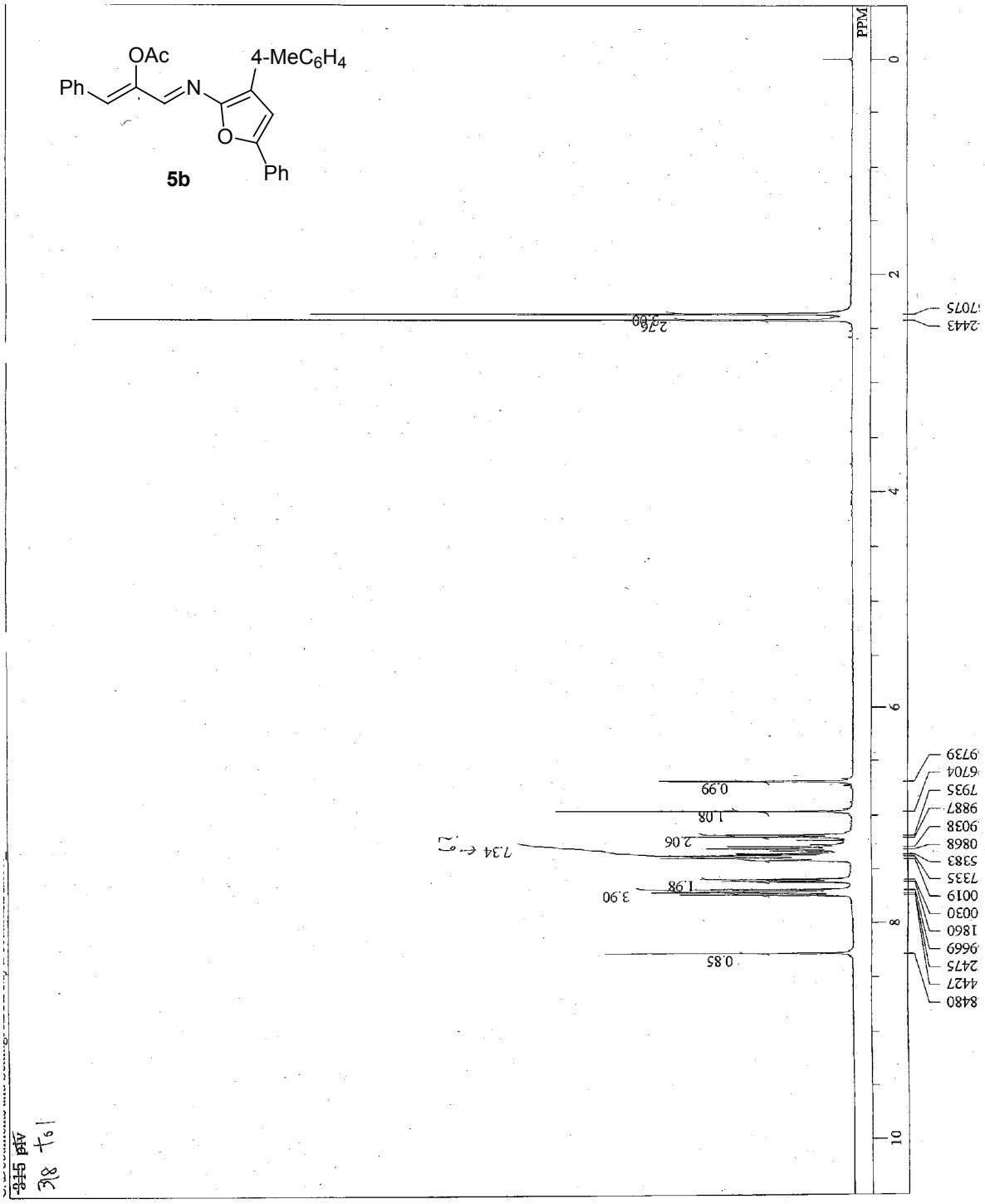
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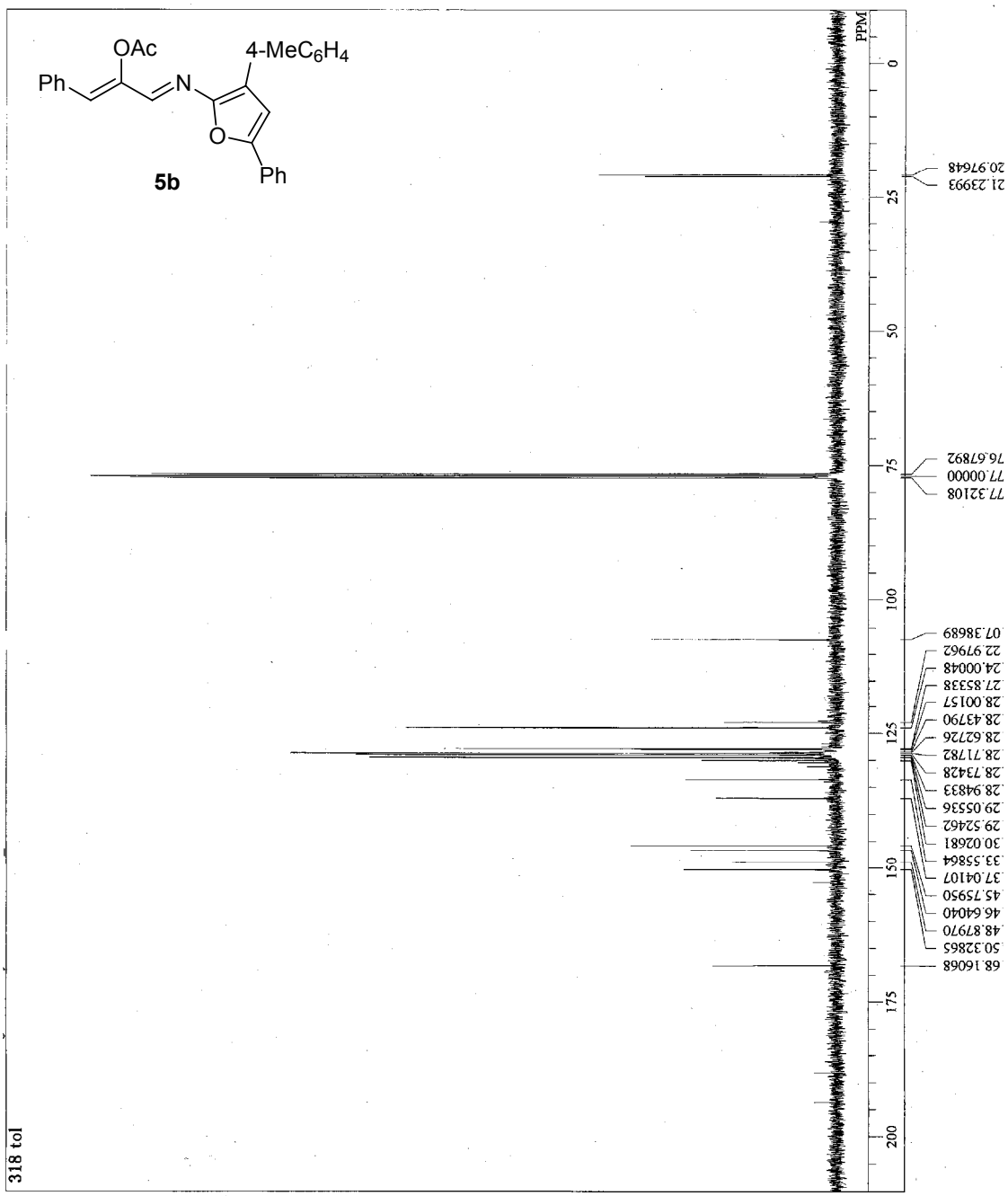
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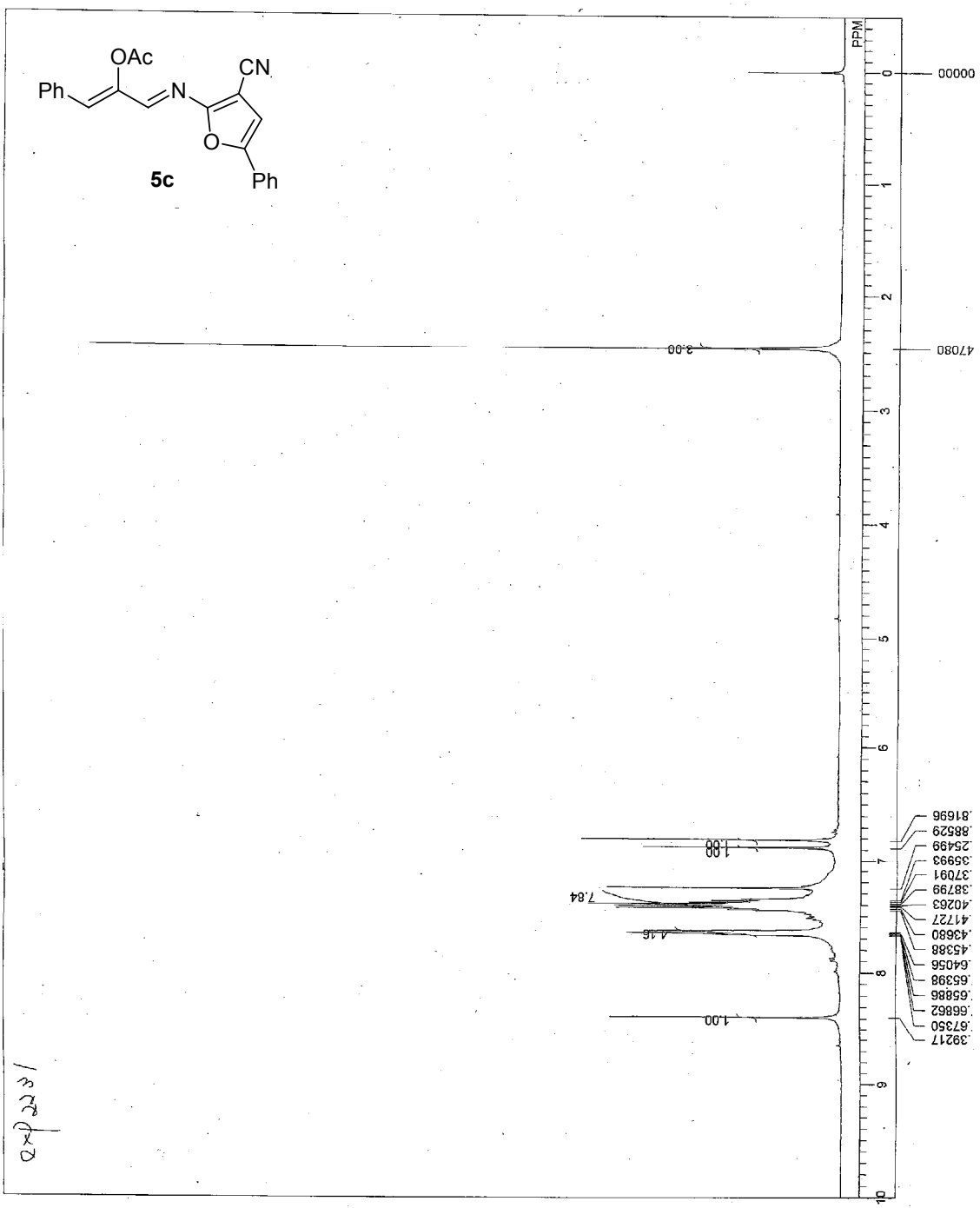
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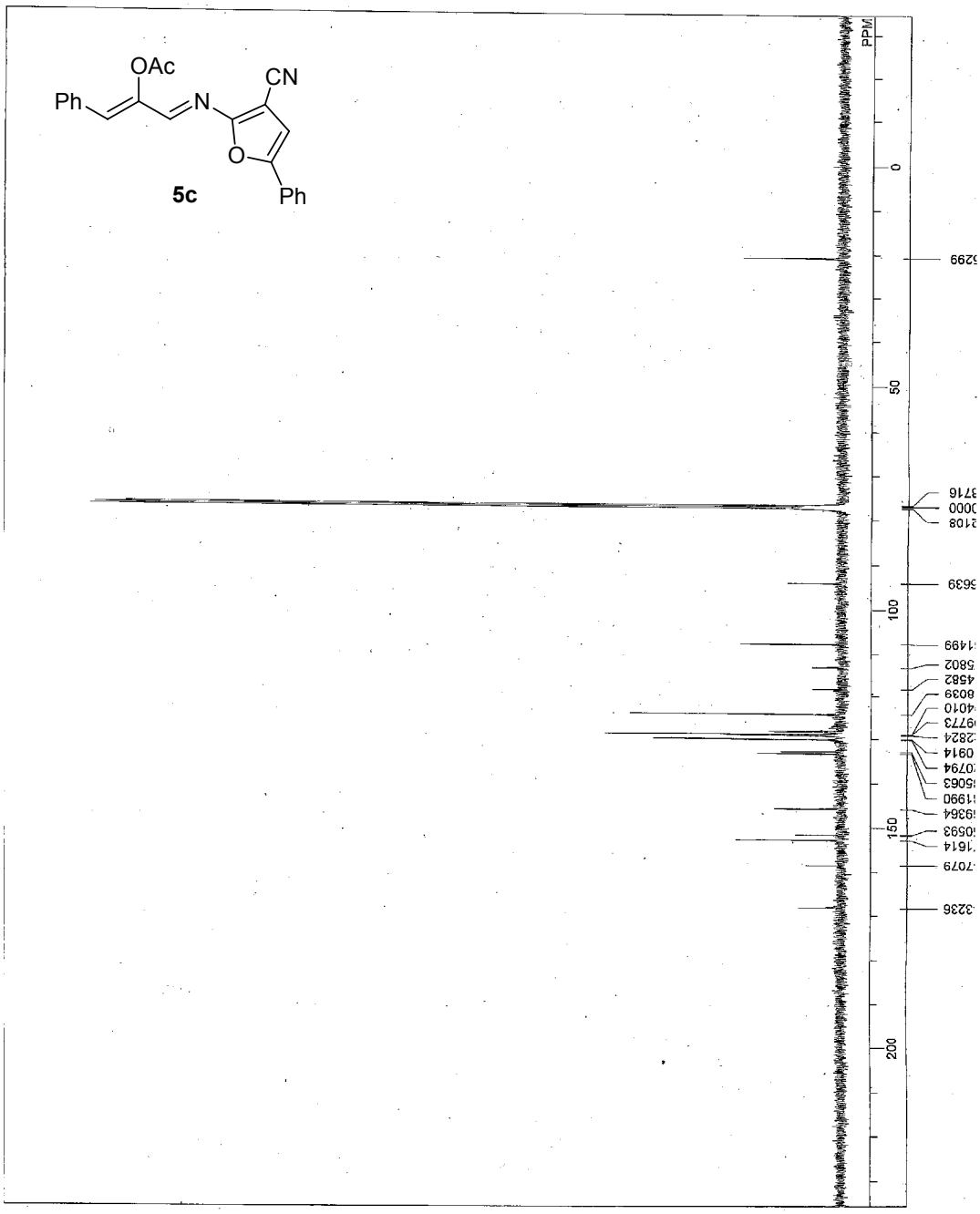
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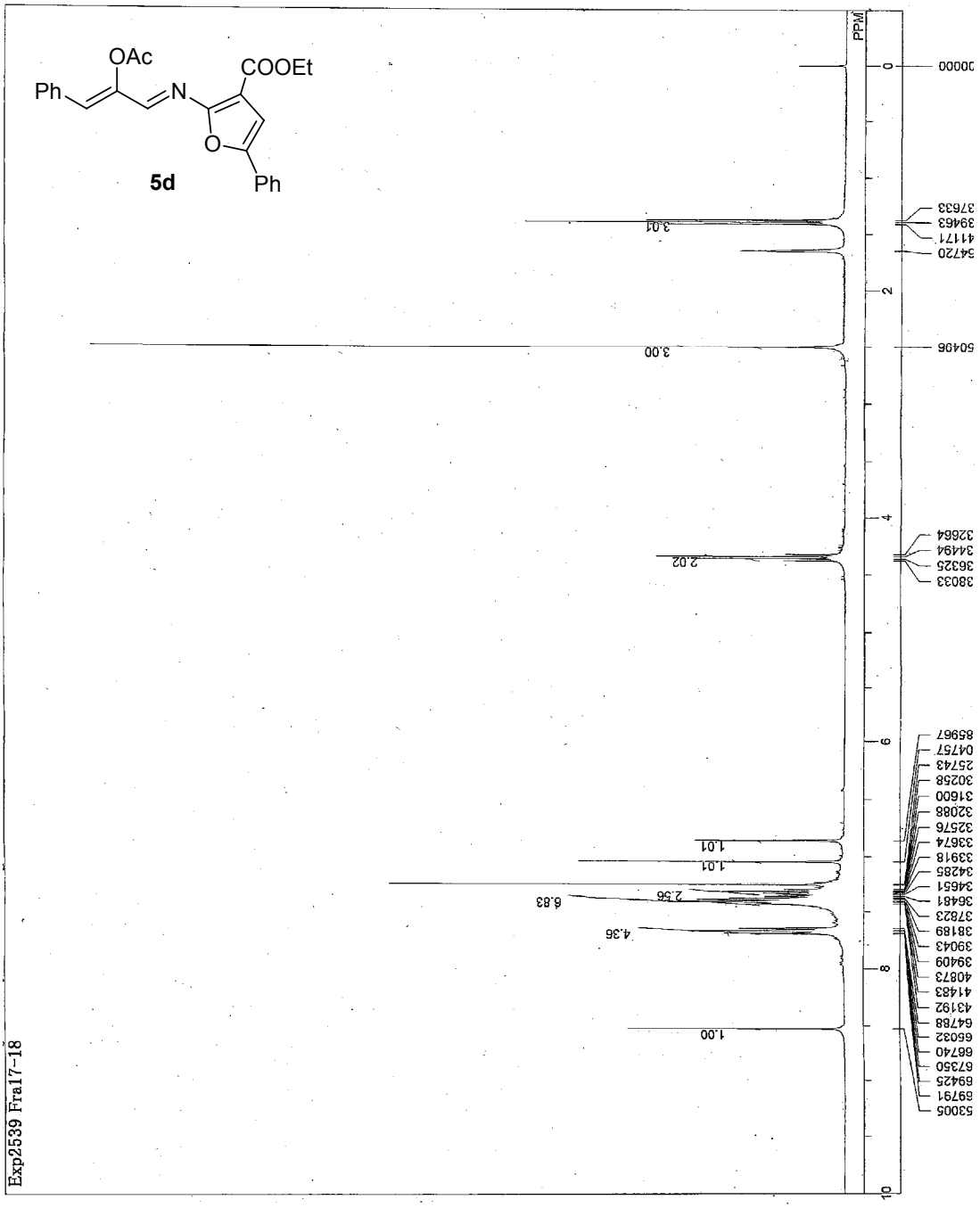
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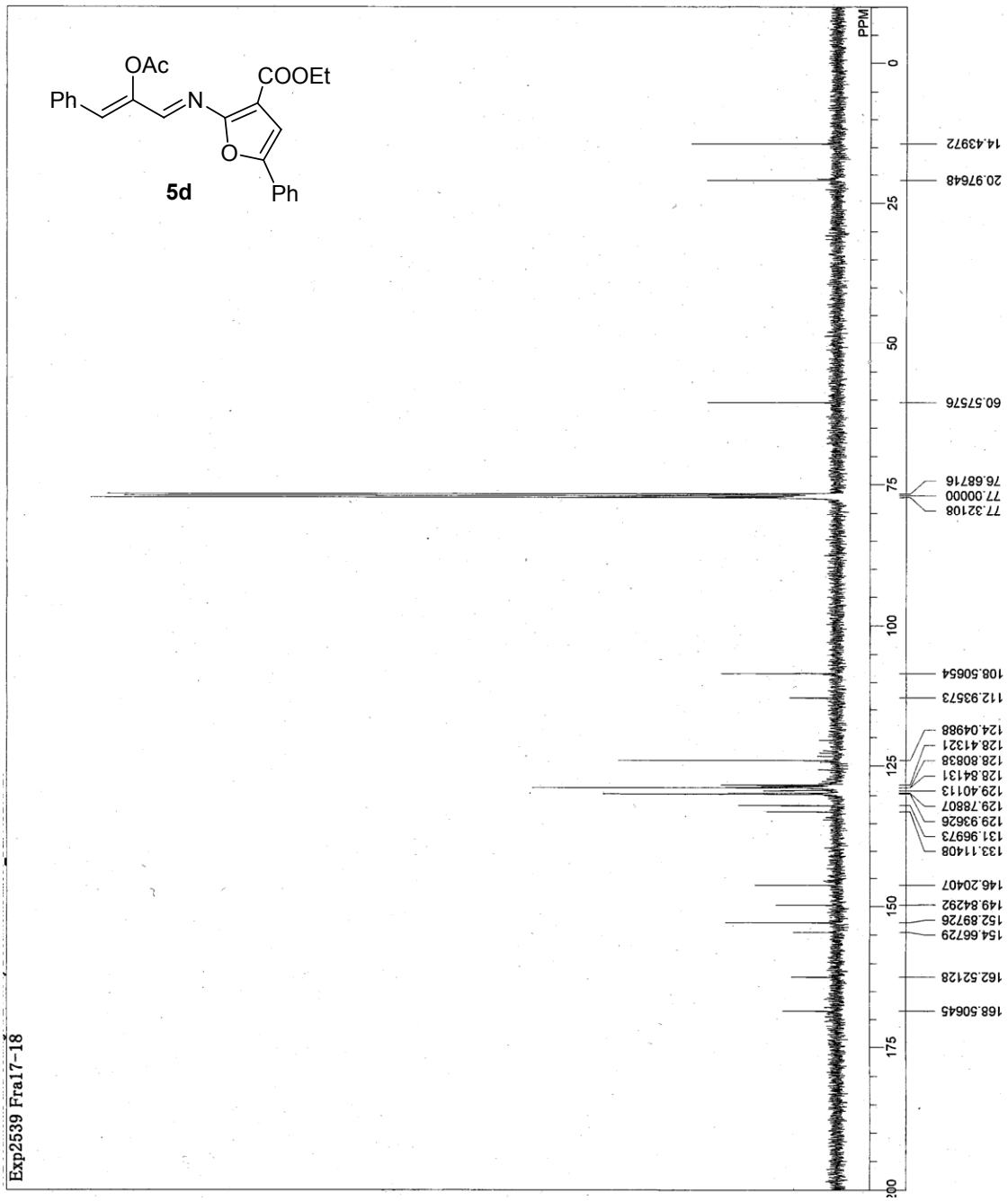
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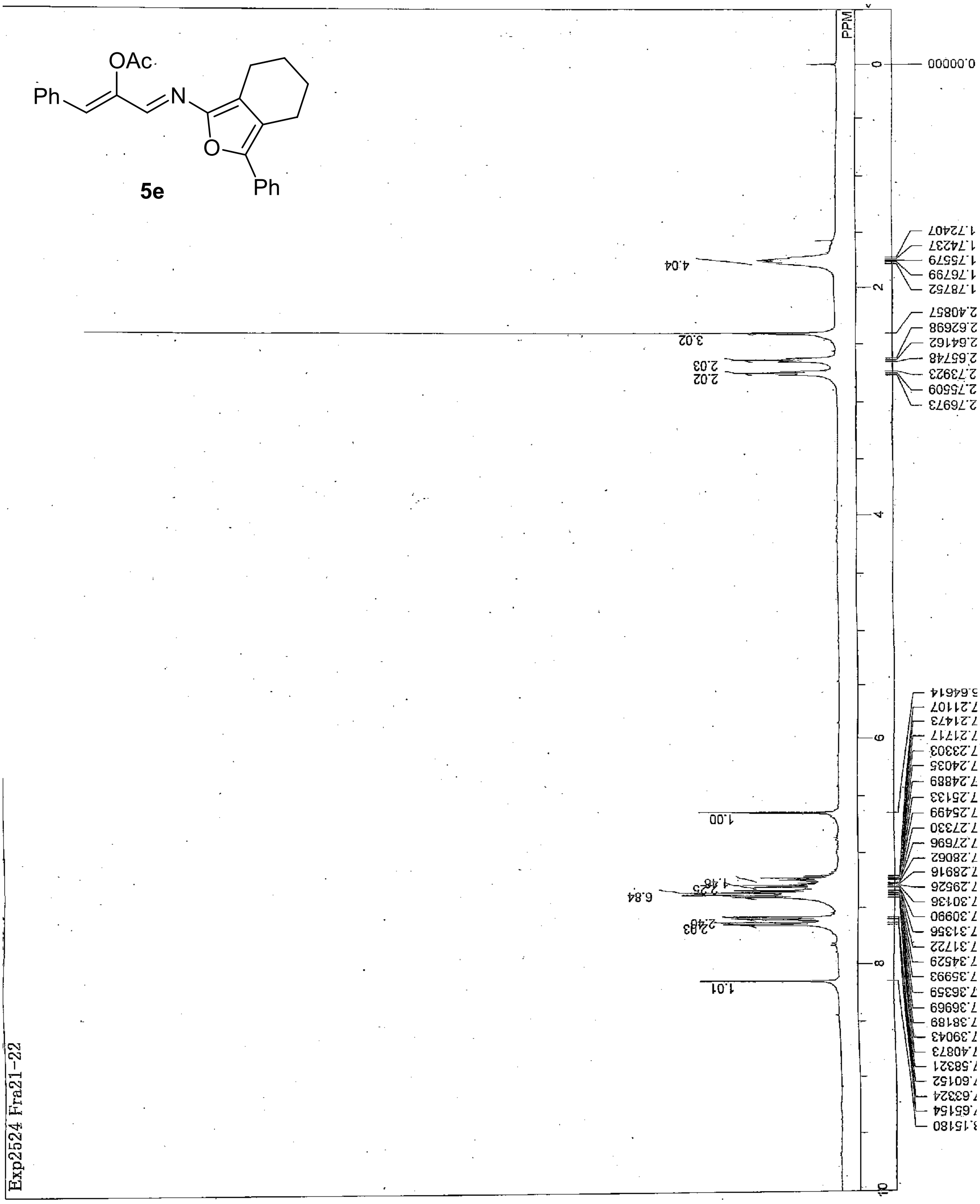
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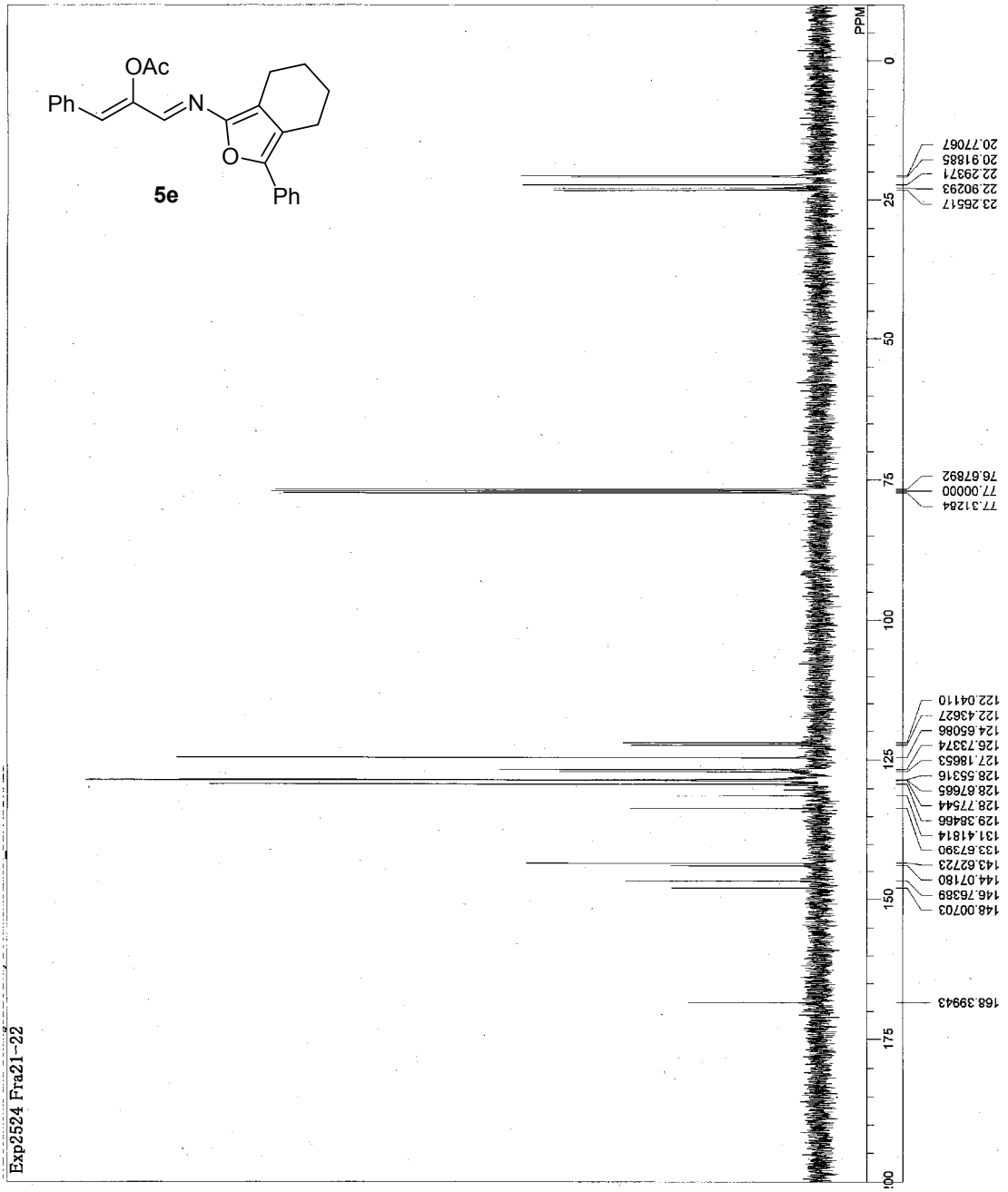
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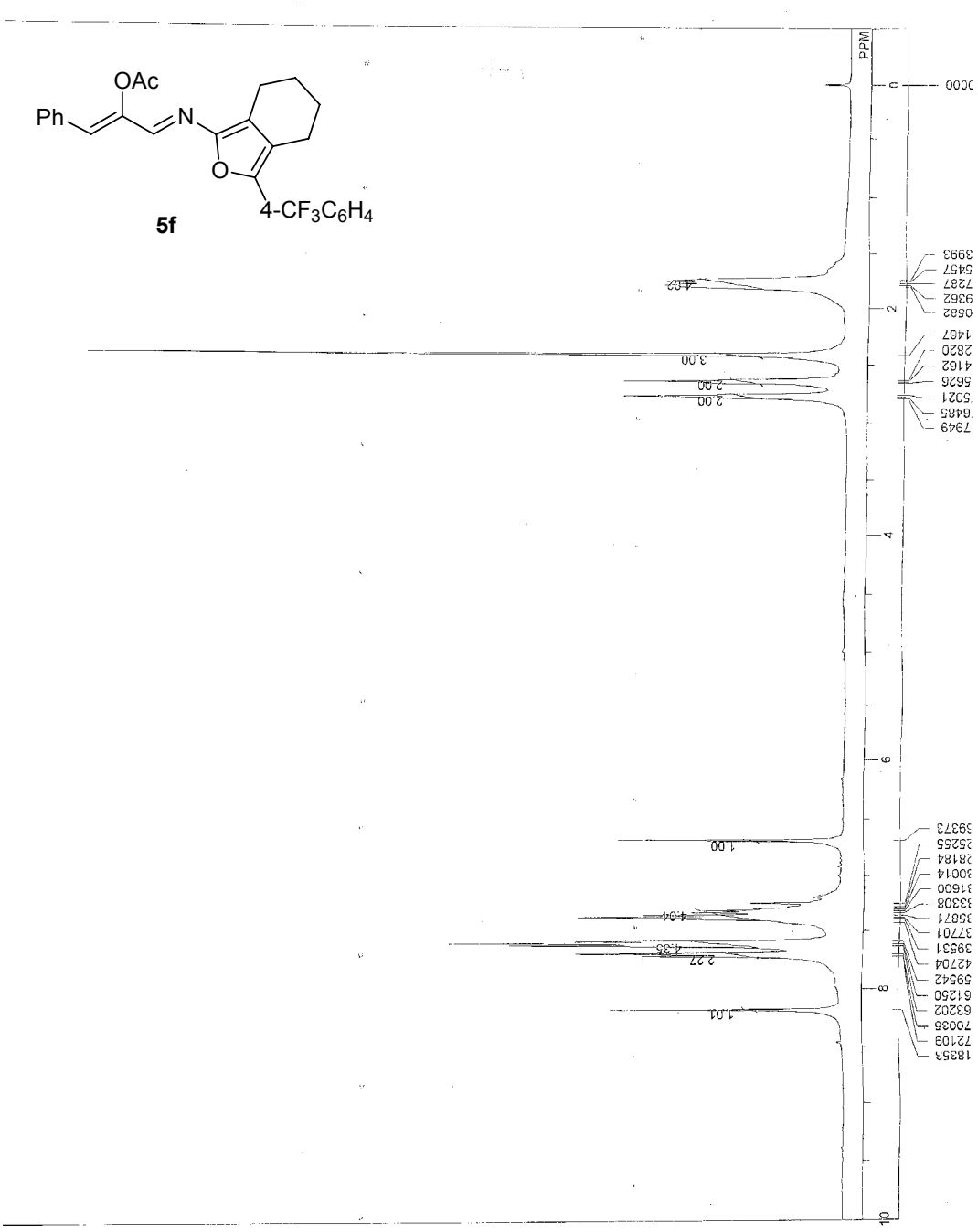
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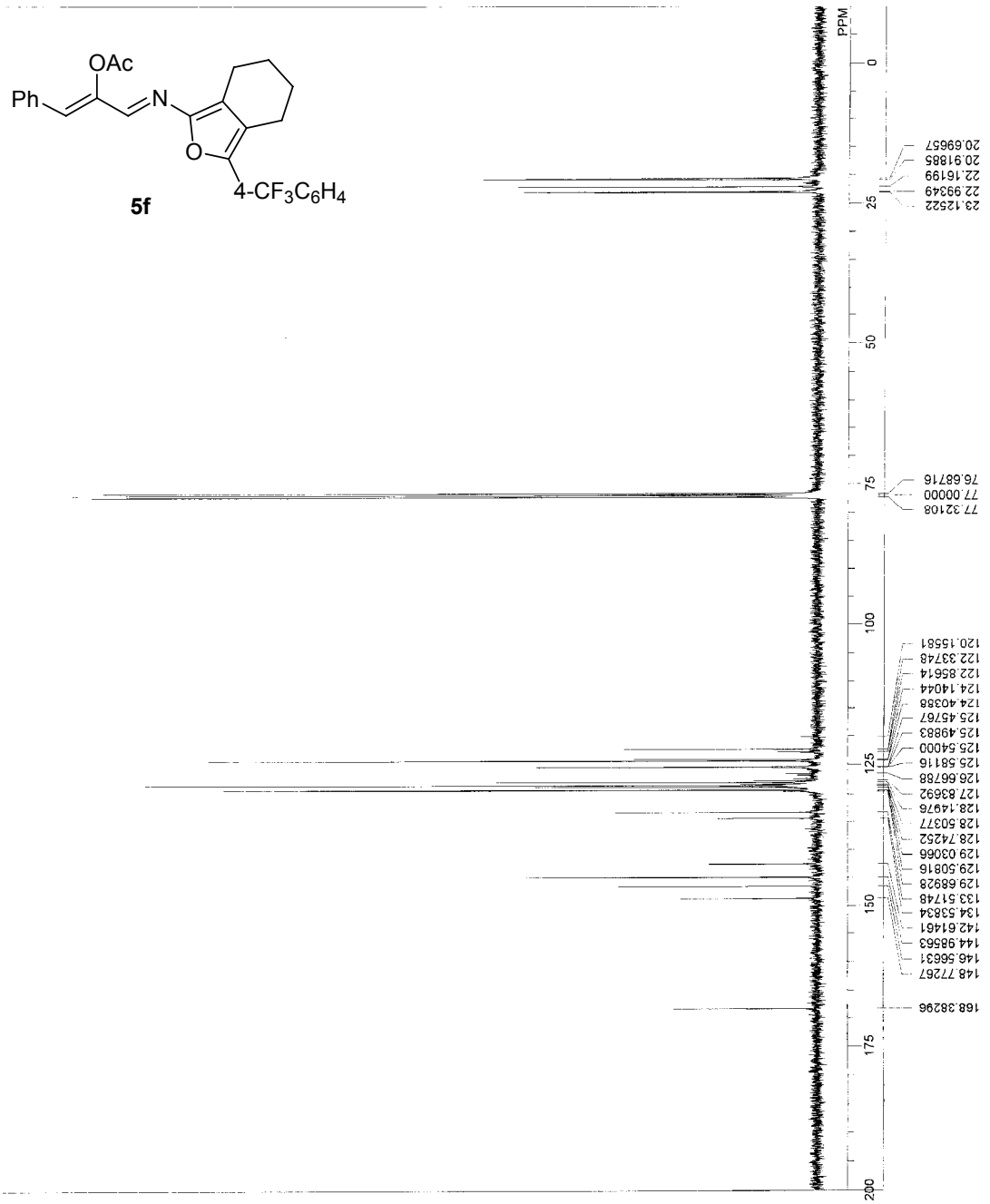
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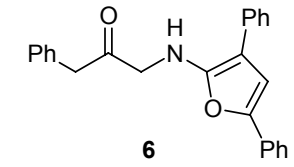

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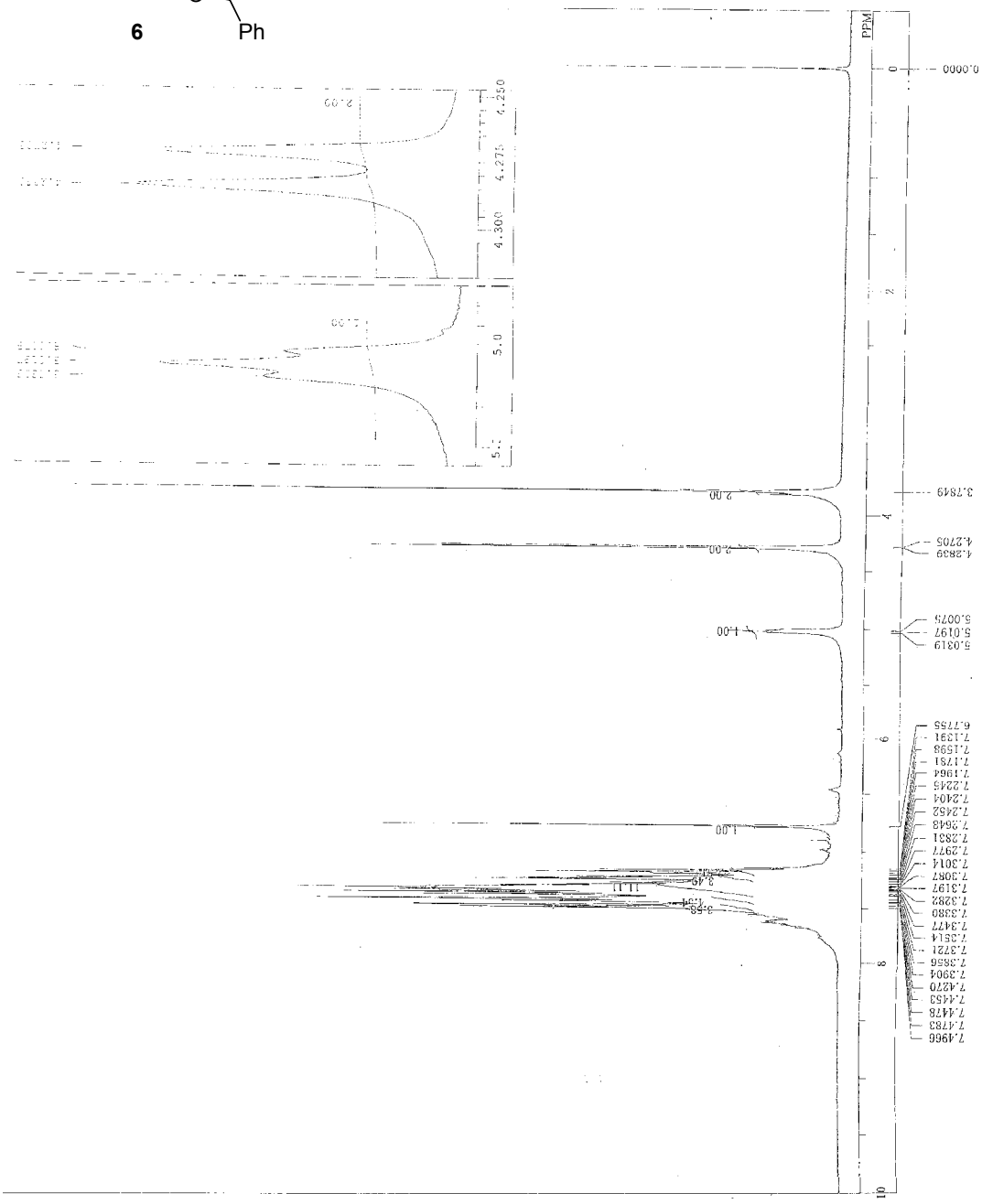

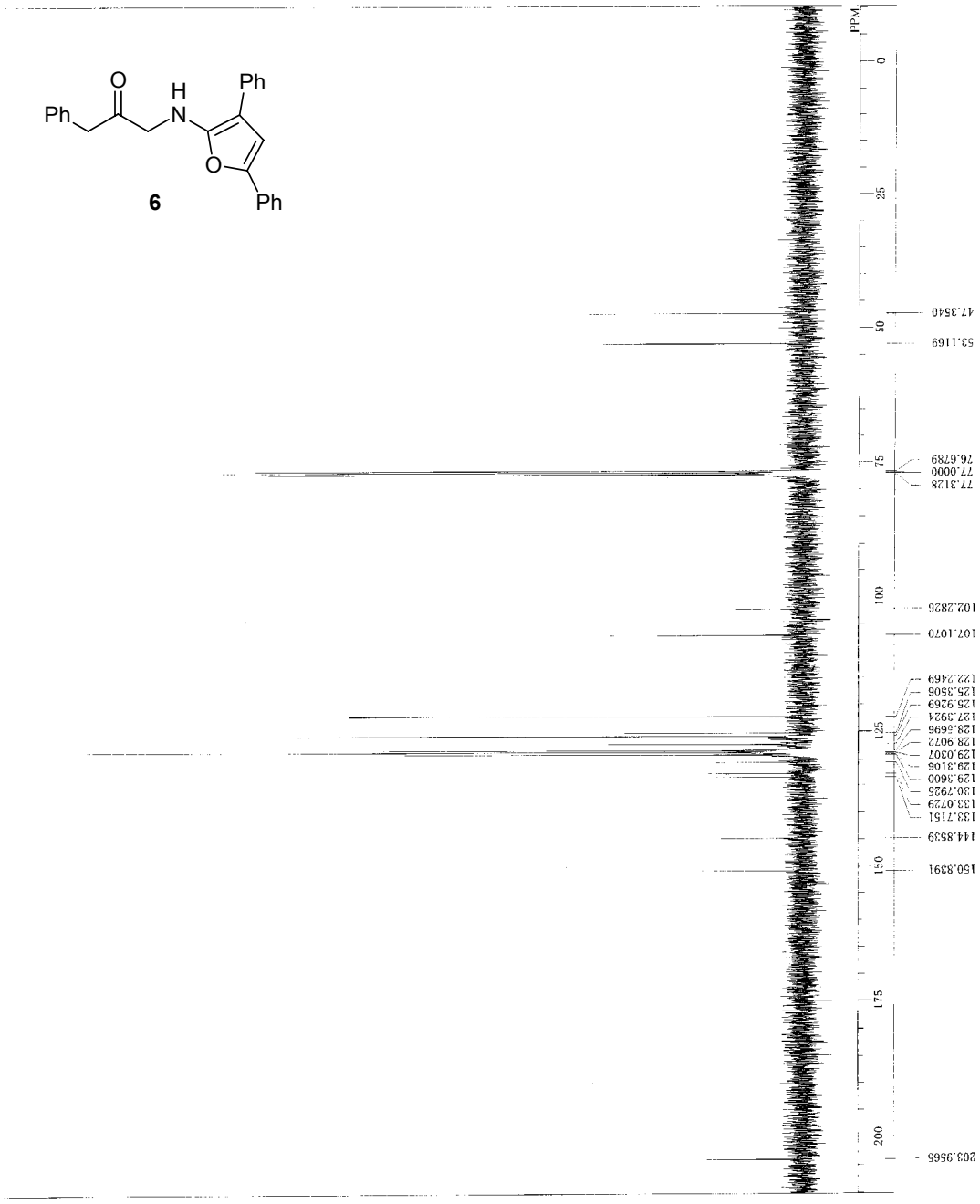
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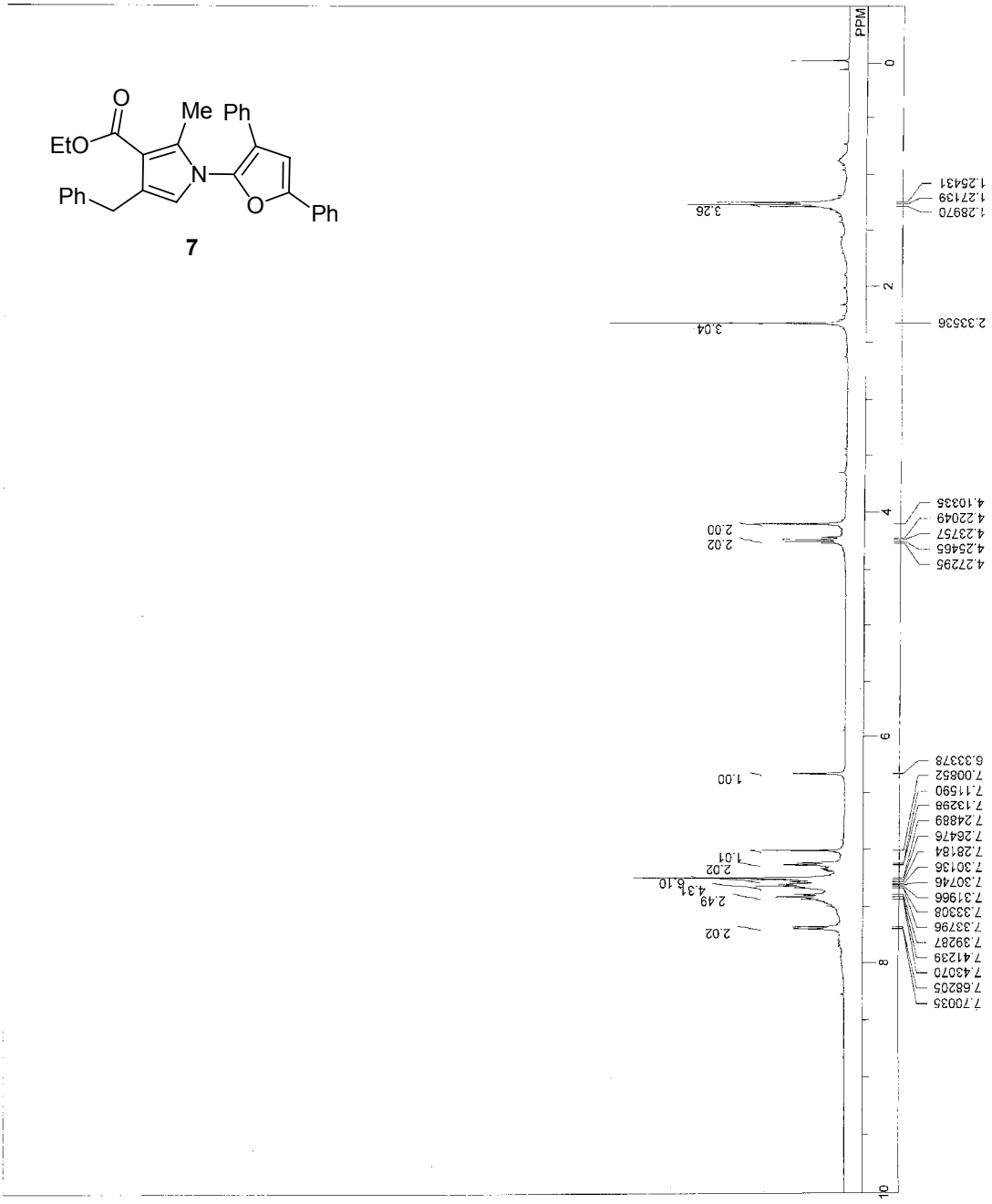
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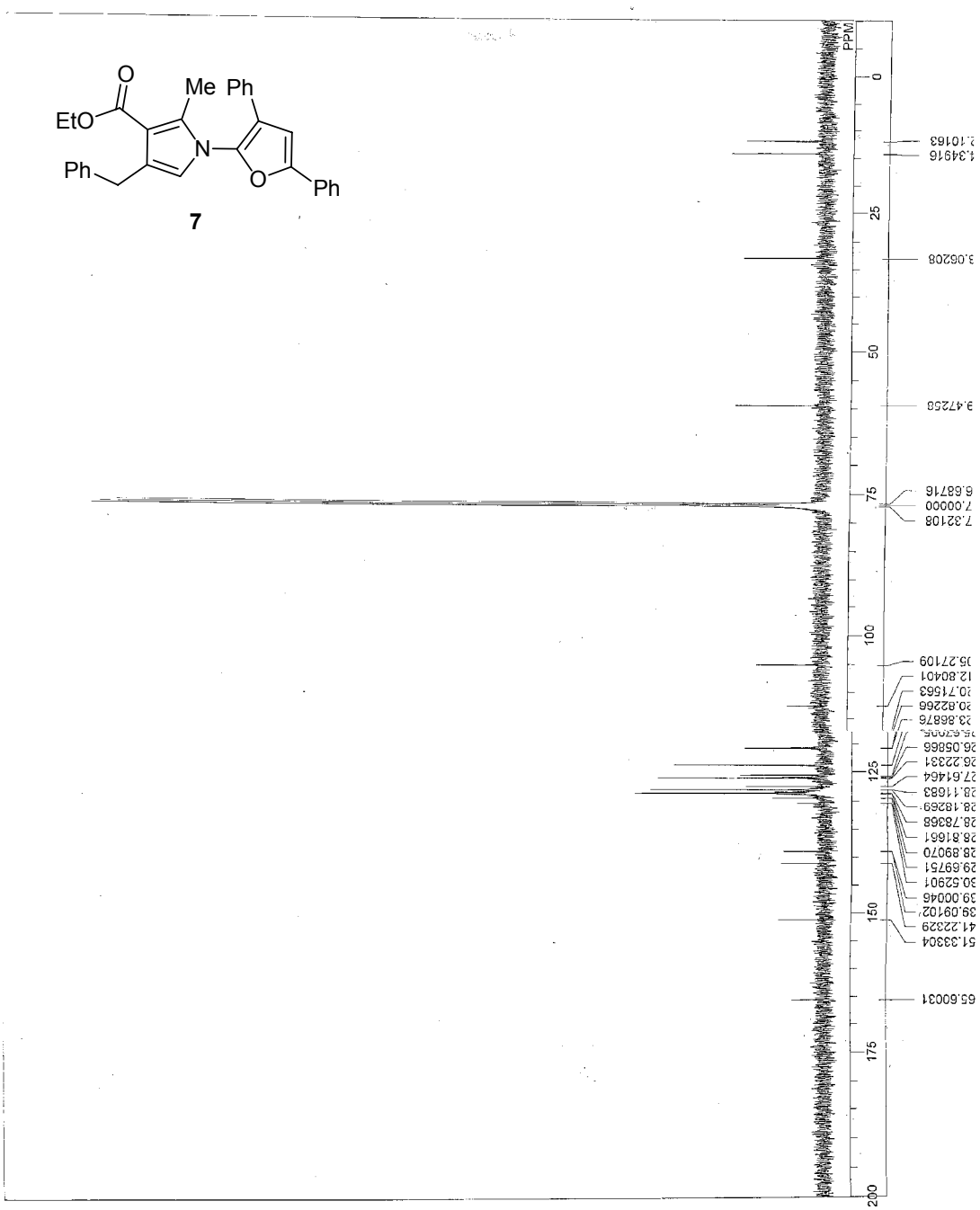
7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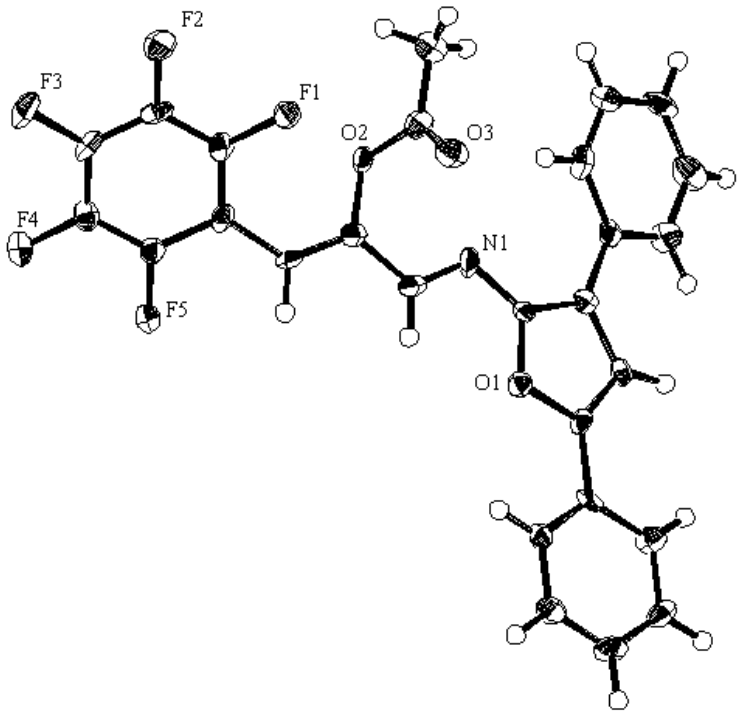
7

X-ray Crystallographic Studies of 3f. Orange crystals of **3f** suitable for X-ray analysis were obtained by recrystallization from $CHCl_3$ /*n*-hexane. The single crystal was sealed in a Pyrex glass capillary under N_2 atmosphere and used for data collection. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo-Kα radiation. Details of crystal and data collection parameters are summarized in Table S1. The positions of non-hydrogen atoms were determined by direct methods (SIR92) and subsequent Fourier syntheses (DIRDIF PATTY). An ORTEP drawing of **3f** is shown in Figure S1. Thermal ellipsoids are displayed at the 50% probability level. The ratio of observed/unique reflections is low (33%) because of poor quality of the crystal. The reflection parameter ratio was more than 10, and we believe that sufficient reflection could be obtained to determine the structure of the product.



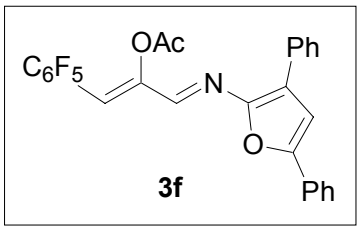


Figure S1. ORTEP drawing of **3f**.

Table S1. Summary of crystallographic data of **3f**

Empirical formula: $C_{27}H_{16}F_5NO_3$

Formula weight: 497.42

Crystal system: monoclinic

Space group: P21/c (#14)

Crystal color: orange

Lattice parameters:

a (Å) = 14.794(6), *b* (Å) = 7.433(3), *c* (Å) = 20.806(8),

V (Å^3) = 2189.0(15), β = 106.905(2)^o,

Z = 4

D_{calc} (g cm^{-3}): 1.509

μ (Mo K α) (cm^{-1}): 1.268

Goodness of fit (GOF) = 1.000

F(000): 1016

Diffractometer: Rigaku RAXIS-RAPID

Radiation: MoK α (λ = 0.71070 Å), Graphite Monochromated

Temp (^{o}C): -150

Scan type: ω–2 θ

Max. 2 θ (^{o}): 55.0

No. of reflections measured total: 4910

No. of observations ($I > 3.00\ \sigma\ (I)$): 14604

Structure solution: Direct Methods (SIR92)

Refinement: Full-Matrix Least-Squares on F

No. of variables: 341

Reflection/parameter ratio: 14.40

Residuals: R = 0.0534, R_{int} = 0.067, R_w = 0.1412

Max Shift/Error in Final Cycle: 0.00

Maximum peak in Final Diff Map (e (Å^{-3}): 0.92

Maximum peak in Final Diff Map (e (Å^{-3}): -0.84